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Niobium-tin-aluminum alloy studies

Thomas Gordon Ellis
Iowa State University

NIOBIUM-TIN-ALUMINUM ALLOY STUDIES

by

Thomas Gordon Ellis

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In Charge of Major Work

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Head of Major Department

Signature was redacted for privacy.

Dean of Graduate College

Iowa State University
Of Science and Technology
Ames, Iowa

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TABLE OF CONTENTS

INTRODUCTION

Niobium is one of the metals being investigated in an effort to develop materials suitable for a variety of high temperature applications. Niobium has a number of properties, such as high melting point, good high temperature strength and creep resistance, moderate density and low neutron capture cross section, that make it potentially useful. However, niobium has low oxidation resistance at elevated temperatures and it is sensitive to embrittlement by interstitial elements. Such behavior imposes severe limitations on its use. The possibility of improving the usefulness of niobium as an engineering material has led to intensive studies of the metal and its alloys in the past few years. Along with these investigations, interest has developed regarding a more comprehensive understanding of the behavior of niobium and its alloys. The investigation reported herein was directed toward the study of the fundamental alloying behavior of certain niobium alloys.

The future of niobium as a useful material most likely will rest upon its alloys rather than on the unalloyed element. Studies have already produced niobium alloys with some properties that are better than those of niobium metal;

but only a few alloys of niobium have been studied in detail. Many of the investigations of niobium alloys were carried out in an effort to supply a particular material for a particular application in a limited amount of time. Only a limited effort could be directed toward ascertaining the fundamental behaviors of the alloys. Consequently many facts concerning such behaviors were overlooked or neglected.

A significant lack of information exists with respect to the binary alloys of niobium with the eleven metals and metalloids in the 3b, 4b and 5b families of the Periodic Table of Elements. At the outset of this investigation only the niobium-aluminum and niobium-silicon binary phase equilibria had been investigated to a point where constitutional diagrams could be proposed. Very limited information on a few other binary combinations of niobium with other elements of these families had been reported.

In view of the interesting properties, especially superconductivity, of the few alloys of niobium with tin and of niobium with aluminum that had been studied and the lack of information on the behavior of other alloys in these systems, the niobium-tin and Nb_3Sn-Nb_3Al alloys were chosen for study. It was anticipated that the results would contribute to the

fundamental knowledge of the alloying behavior of niobium as well as possibly leading to the development of useful niobium alloys.

HISTORY AND OCCURRENCE

Niobium was first discovered in 1801 by Hatchett, an English chemist, in an ore from Connecticut. He named the new element columbium for the country* in which the ore was found. In 1844, Rose, another English chemist, discovered a new element in a tantalite ore. He named the new element niobium**. Eventually the "columbium" of Hatchett and the "niobium" of Rose were shown to be the same element. At the Fifteenth International Union of Chemistry Congress held in Amsterdam, The Netherlands in 1949 niobium was adopted as the name for element 41. However, the name columbium continues to be preferred by most American producers of the metal (1).

Niobium occurs principally in two ores, columbite $(Fe,Mn)O\cdot(Nb,Ta)_2O_5$ and pyrochlore $(Na,Ca)\cdot Nb_2O_6F$, although many other niobium minerals are found throughout the world (1). Of the two principal ores columbite has been the chief source of niobium; but the percentage of total known niobium reserves existing as pyrochlore greatly exceeds that in the

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*Columbia, another name for America.

**For Niobe, daughter of Tantalus; Greek Mythology.

columbite deposits. Therefore, pyrochlore could become increasingly important as a source of niobium.

Tin, one of the seven metals of antiquity, was first used by ancient cultures in the preparation of bronze, a copper-tin alloy. The use of tin in bronze predates the first preparation of metallic tin by more than 500 years (2). Even to the present time tin has continued to be used primarily as an alloying constituent or a coating.

Tin is never found in nature in the native or metallic state even though it is considered to be a relatively unreactive metal. It is generally found in combination with oxygen in a mineral called cassiterite (SnO_2) or as stannite, a complex sulfide of tin and copper and iron. Of these two ores only cassiterite is industrially important (3).

The first reported preparation of a niobium-tin alloy was by Mattias, et al. (4) of the Bell Telephone Laboratories in 1954. They were particularly interested in the properties exhibited by A_3B type intermetallic compounds in view of the reported superconducting behavior of V_3Si. By analogy, they assumed that niobium and tin would form a similar compound. Their objective then was to prepare Nb_3Sn and study the crystal structure and superconducting behavior of this com-

pound. They reported that tin reacts peritectically with niobium between 1200°C and 1550°C to form this intermetallic compound. Nb_3Sn was found to be simple cubic (Cr_3O) having a lattice constant of about a = 5.3 A. A sharp transition from the normal to the superconducting state was observed at 18.05°K, the highest zero field superconducting transition temperature (T_c) of any material then reported. Geller, et al. (5), later, reported the lattice constant of Nb_3Sn to be 5.297 $\pm$ 0.002A, which gave a calculated density of 8.92 gm/cc for the compound.

A binary equilibrium diagram for niobium-tin alloys was proposed by Agafonova, et al. (6) in 1959. They concluded that:

1. Nb_3Sn, reported earlier by Mattias, et al., was the only intermetallic compound formed in the niobium-tin system and it decomposed peritectically into niobium and tin at 2000 $\pm$ 25°C.
2. Alloys of 60 weight per cent tin and greater had a liquid immiscibility gap within a narrow temperature range above 730 $\pm$ 5°C.
3. The solubility of tin in niobium was 9.7 weight per cent at room temperature and increased to

14 weight per cent at 2000 $\pm$ 25^{o}C.

In an extention of the investigation at Bell Telephone Laboratories on compounds of the A3B type, Wood, et al. (7) in 1958 reported the preparation of Nb_3Al. The crystal structure of this compound was found to be simple cubic (Cr_3O) with a lattice constant of a = 5.187 A. They observed that Nb_3Al had a zero field superconducting transition temperature (T_c) of 17.5^{o}K.

GENERAL PLAN OF THE INVESTIGATION

When the investigation of the niobium-tin and some niobium-tin-aluminum alloys was initiated late in 1960 the information found in a literature search was confined to that in the reports on Nb_3Sn by Mattias, et al. (4) and Geller, et al. (5) and to the report on Nb_3Al by Wood, et al. (7). At the outset four main objectives were proposed for the investigation:

1. To develop methods suitable for preparing all niobium-tin alloys and the niobium-tin-aluminum alloys of interest.
2. To determine the equilibrium phase relationships for the niobium-tin alloys.
3. To study the crystallography of the new niobium-tin phases which were predicted for this alloy system.
4. To study the superconducting behavior as well as the crystallography of the system between the two superconducting compounds, Nb_3Sn and Nb_3Al.

A number of facts relevant to the proposals for this investigation were given preliminary consideration. First, with respect to alloy preparation, it was strongly suspected

that some difficulty could be encountered in attempting to alloy niobium and tin. Niobium has a very high melting point while tin has a low melting point. In fact, tin boils at a temperature about 200 centigrade degrees below the melting point of niobium. At very high temperatures niobium reacts with essentially all container materials including refractory oxides, other high melting point metals, graphite, and refractory carbides. Therefore, comelting the two components, niobium and tin, in a crucible would be impractical due to the high vapor pressure of tin at the melting point of niobium and the lack of a suitable container.

Preparing alloys by "skull" melting techniques such as non-consumable arc melting seemed impractical for all but those alloys having a very high niobium content. "Skull" melting necessitates that the alloy be in contact with a relatively cool surface in order to keep a solid skin of the alloy between the molten pool and the hearth during melting. If the mixture charged to the arc melter contained any more than a few per cent tin it was suspected that the heat generated by the arc would not dissipate fast enough from the liquid tin phase to permit a solid skin to form. Furthermore, it was doubtful that niobium could be melted satis-

factorily in molten tin in an arc melter.

Therefore, it was evident that much more complex methods would have to be developed in order to overcome the difficulties of preparing alloys of niobium-tin and, likewise, niobium-tin-aluminum.

A few generalizations could be made about the solid state phase relationships of niobium-tin alloys. Niobium has a body centered cubic crystal structure while tin has a diamond cubic crystal structure below 18°C and a tetragonal crystal structure from 18°C to its melting point (8). Since tin and niobium have these different crystal structures a complete miscibility in the solid state seemed impossible. The solid solubility of one component in the other based on the Hume-Rothery size criterion could be appreciable since the atomic radii of niobium and tin differ by only three per cent (9). However, comparing the niobium-tin system with similar binary systems, such as zirconium-tin, niobium-germanium and niobium-silicon (10), a very limited solid solubility (less than 0.5 per cent) of niobium in tin would be expected while the solid solubility of tin in niobium could be as high as 5-10 per cent.

One intermetallic compound, Nb_3Sn, had been reported

previous to the initiation of this investigation. Again, based on the similar alloy systems listed above, at least one and possibly more than one additional intermetallic compound would be expected in the niobium-tin system. The existence of compounds in addition to Nb_3Sn was verified very early in the investigation by examining diffusion couples between niobium and tin prepared at several different temperatures. At least one additional compound was definitely recognized. This fact was well established before the report of Agafonova, et al. (6) became available and was in direct disagreement with one of their conclusions.

The intermetallic compounds of niobium with tin and with aluminum, Nb_3Sn and Nb_3Al, have zero field superconducting transformation temperatures (T_c) that are higher than those for most other measured materials. A literature survey revealed very little information that showed any general trend in the T_c values with composition for alloys of two such compounds. Also, no general principles on which to base any prediction of the superconducting behavior of alloys of such systems could be found. In view of the outstanding superconducting properties of these two compounds and their closely related crystal structures, it seemed possible that

a study of the superconducting behavior of alloys of these compounds could reveal pertinent information regarding the phenomenon of superconductivity.

Since Nb_3Sn and Nb_3Al have the same Cr_3O type crystal structure and lattice constants that differ by only 2 per cent it would be expected that Nb_3Sn and Nb_3Al would be completely miscible in each other. It was also expected that the lattice constants of the alloys would follow Vegard's rule, that is, the lattice constants of the alloys would be linear with composition between those of the pure components.

MATERIALS

Two forms of niobium metal, granules and powder, were used in preparing the niobium-tin and niobium-tin-aluminum alloys. The granular niobium was supplied by E. I. DuPont de Nemours and Company as their Grade D-3 Columbium. The individual particles were spherical in shape, -20 +35 mesh in size. A typical chemical analysis of some impurities in granular niobium as supplied by the producer was as listed in Table 1.

Table 1. Impurities in DuPont D-3 granular columbium

Impurity	Impurity Concentration
Carbon	~10 ppm
Oxygen	~100 ppm
Nitrogen	~10 ppm
Tantalum	<500 ppm

The niobium powder was supplied by the Electro Metallurgical Corporation. The analysis of impurities issued by the producer was as listed in Table 2.

Table 2. Impurities in Electromet Nb metal

Impurity	Impurity Concentration
Carbon	340 ppm
Oxygen	600 ppm
Hydrogen	250 ppm
Nitrogen	190 ppm
Tantalum	500 ppm
Iron	600 ppm
Nickel	100 ppm

Two forms of tin were used in preparing the niobium-tin and niobium-tin-aluminum alloys. Where possible, massive tin from 1 pound block tin ingots produced by the National Lead Company was used. Although no analysis of the block tin was available the tin was thought to be 99.9+ per cent pure. In cases where finely divided tin was required, granular tin supplied by the J. T. Baker Chemical Company was used. A typical analysis supplied with the granular tin was as listed in Table 3.

Niobium pentoxide (Nb_2O_5) used in the preparation of Nb_3Al was supplied by the Fansteel Metallurgical Corporation

as "High Purity Columbium Pentoxide." The only impurity level listed by the producer was that the pentoxide contained less than 500 ppm tantalum.

Table 3. Impurities in Baker granular tin

Impurity	Impurity Concentration
Arsenic	0.2 ppm
Copper	5 ppm
Iron	30 ppm
Lead	30 ppm
Zinc	5 ppm

Aluminum powder used to prepare Nb_3Al was Grade 120 Atomized Aluminum produced by the Aluminum Company of America. No analytical data on the impurity content of this material was received from the producer. Chemical analyses performed at Ames Laboratory gave the uncombined aluminum content of the powder as 94.1 weight per cent and the carbon content as 80 ppm.

Qualitative spectrographic analyses of all materials used in this investigation were performed at Ames Laboratory. The results of these analyses are listed in Table 4. Only

those elements actually detected are listed in the table.

Table 4. Qualitative spectrographic analysis of materials

Material	Elements found in various spectrographic intensity ranges				
	Weak	Very weak	Trace	Faint trace	Very faint trace
DuPont D-3 Granular Columbium			Fe	Ge Mg Mn Ni	
Electromet Nb Metal		Fe Mg Ni	Cu	Ag Si	Pb
Baker Granular Tin		In	Fe Sb	Ca Cu Mg Ni Pb Si	
Block Tin		Cu Pb	Fe In Mg Sb	Cr Ni Si	V
Grade 120 Atomized Aluminum		Fe Si	Cu Mg Mn	Ag Ca Ti V	Ni Zr
Fansteel Nb_2O_5			Fe Mg Si	Ca Mn Ni	Pb

EXPERIMENTAL PROCEDURES AND DATA

Alloy Preparation Methods

Due to the extremely high melting point of niobium as compared to that of tin and aluminum, no single method of alloy preparation was adaptable to all alloy concentrations. The methods employed depended largely upon the desired composition of the alloys. In some cases, however, alloys of the same composition were prepared by more than one procedure depending upon the desired forms of the specimens for specific measurements. The techniques employed in the preparation of the alloys are exemplified in the following descriptions.

Preparation of Nb_3Sn

The intermetallic compound Nb_3Sn was prepared by heating niobium pellets in molten tin to allow the reaction:

$$3Nb + Sn \longrightarrow Nb_3Sn$$

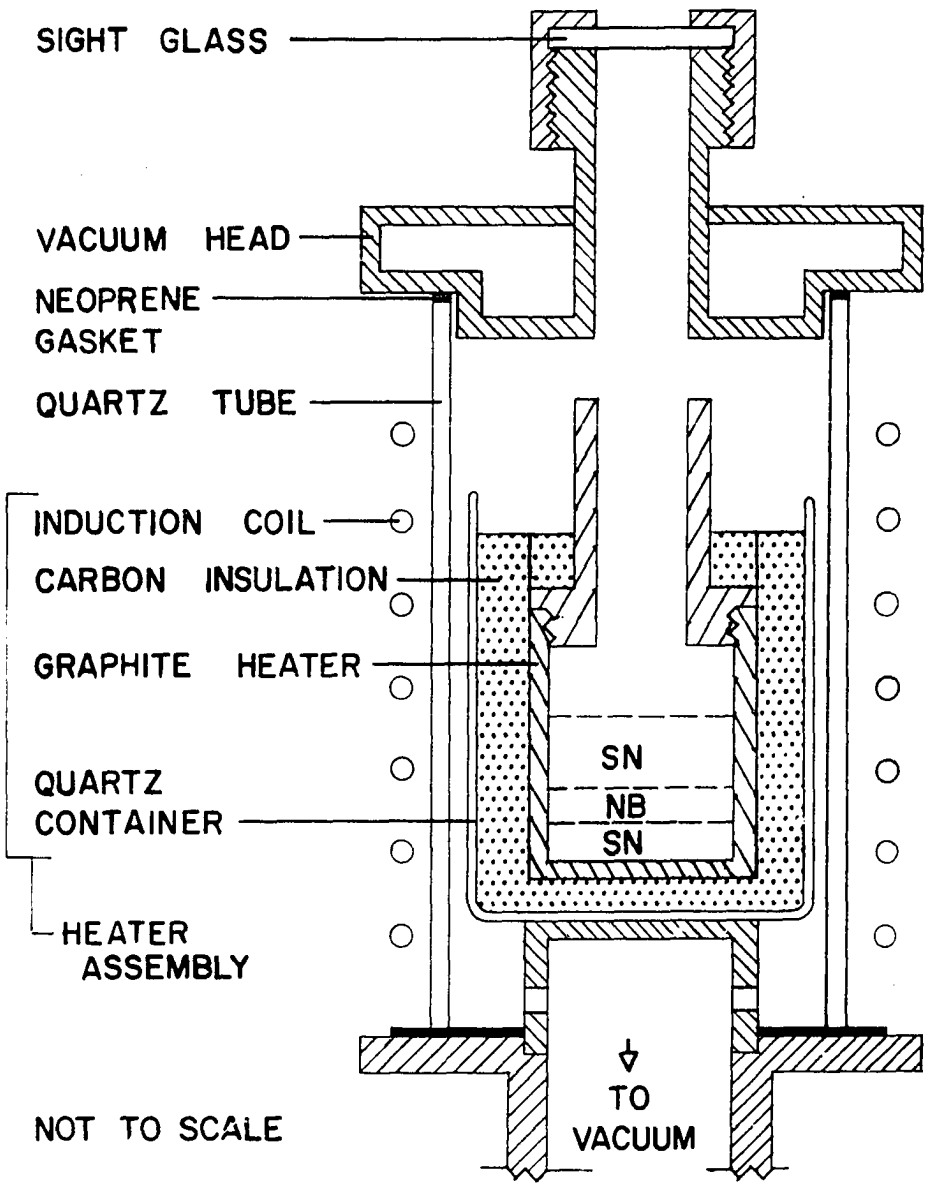
to take place. Although the stoichiometry of this reaction suggests a charge containing 29.6 weight per cent tin, it was found that 75 to 85 weight per cent tin was required in the charge to obtain a complete reaction of all of the niobium in a reasonable time interval at the temperature

employed. Also, charges of near stoichiometric composition caused fracture of the crucibles. This fracturing was probably due to sintering of the agglomerated niobium pellets followed by expansion during reaction with the tin.

The following procedure for preparing Nb_3Sn was found to be reliable. First, a quantity of tin was melted, poured into a thin walled graphite crucible to a depth of approximately one inch and allowed to solidify. The niobium granules were then placed in the crucible on top of the solidified tin. The remaining tin to be charged was then melted and poured into the crucible and allowed to cool. Preparing the charge in this manner tended to reduce the agglomeration of the niobium pellets during subsequent melting of the tin. A typical charge contained 250 grams of niobium and 1350 grams of tin.

An induction heater assembly (see Figure 1) was constructed by placing the graphite crucible containing the charge in a fused quartz beaker large enough to permit at least 1/2 inch of carbon black insulation between the graphite crucible and the quartz beaker. For induction heating, the graphite crucible not only served to contain the charge but also served as the principal heater element.

Figure 1. Vacuum induction furnace used to prepare Nb_3Sn.


SIGHT GLASS
VACUUM HEAD
NEOPRENE GASKET
QUARTZ TUBE
INDUCTION COIL
CARBON INSULATION
GRAPHITE HEATER
QUARTZ CONTAINER
HEATER ASSEMBLY
SN
NB
SN
TO VACUUM
NOT TO SCALE

The induction furnace used to heat the charge consisted of a 40 turn 4 1/2 inch diameter water cooled copper coil surrounding a 4 inch diameter fused quartz tube. The tube was connected through a valve to a vacuum system capable of pumping 350 liters of gas per second at 0.1 microns of mercury pressure and having an ultimate pressure of approximately 0.001 microns of mercury. The coil was powered with a 6 kilowatt Ajax mercury-arc converter.

The induction heater assembly containing the charge was placed within the induction coil of the furnace. The system was evacuated and the power was turned on. The charge was heated in vacuo essentially by the heat generated through induction heating of the graphite crucible. Upon reaching 1500°C the power supply was adjusted so that the temperature within the reaction crucible remained at about 1500°C under steady inductive power input. This temperature was "as observed" through the sight glass with a disappearing filament optical pyrometer. The induction eddy currents within the charge caused a violent agitation of the molten metal. The agitation could be readily observed through the sight glass. The reaction charge was held at this temperature for 8 hours after which the power was turned off and the

charge allowed to furnace cool in vacuo to room temperature.

After cooling, the crucible was removed from the heater assembly. The graphite crucible was broken away from the niobium-tin alloy and the alloy was placed in 12 N. hydrochloric acid. The acid leached away the uncombined tin leaving a niobium-tin alloy residue. Chemical analysis of this residue for niobium content by the peroxide colorimetric method (11) gave a niobium concentration of only 50.75 weight per cent, however, instead of the 70.4 weight per cent niobium for Nb_3Sn.

The residue contained two distinct forms of particles. One form was that of rough surfaced spheres slightly larger than the niobium granules originally charged, while the other was that of distorted hexagonal platelets. On the basis of the chemical analysis and the observed particles it appeared that at least one other compound richer in tin than Nb_3Sn was present in the leached alloy residue.

Compounds other than Nb_3Sn were eliminated from the residue by heating it in vacuo for 2 hours at $1000^{o}C$ followed by quenching in water. This heat treated alloy was then leached with hydrochloric acid to remove any free tin. This residue contained the rough surfaced spheres of

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After cooling, the crucible was removed from the heater assembly. The graphite crucible was broken away from the niobium-tin alloy and the alloy was placed in 12 N. hydrochloric acid. The acid leached away the uncombined tin leaving a niobium-tin alloy residue. Chemical analysis of this residue for niobium content by the peroxide colorimetric method (11) gave a niobium concentration of only 50.75 weight per cent, however, instead of the 70.4 weight per cent niobium for Nb_3Sn.

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the original residue but it did not contain any hexagonal platelets.

Chemical analysis of this final residue for niobium content by the peroxide colorimetric method (11) gave a niobium concentration of 70.0 weight per cent (Nb_3Sn is 70.4 weight per cent niobium). X-ray diffraction analysis of this product by the Debye-Scherrer powder method showed it to be simple cubic with a lattice constant of a = 5.29 A. This lattice constant and the intensities of the diffraction lines were consistent with the data reported by Geller, et al. (5) for Nb_3Sn. All of the Nb_3Sn used in this investigation was prepared in this manner.

Preparation of alloys richer in niobium than Nb_3Sn

Alloys having niobium concentrations higher than Nb_3Sn were prepared by non-consumable arc melting of niobium-Nb_3Sn compacts under helium at atmospheric pressure. These compacts were prepared by thoroughly mixing niobium and Nb_3Sn powders and pressing the mixtures into 1/4" x 1/4" x 3" bars at 53,500 psi. The "green" strength of the bars was sufficient to permit careful handling without crumbling. Each bar was melted four times, once from each of its four sides, to give the final solid bar of alloy.

Prior to melting the samples, the arc-melting chamber was flushed five times with helium gas by reducing the melting chamber pressure to less than 25 microns of mercury, isolating the chamber and refilling it to atmospheric pressure with helium. Subsequent to the last helium flush but prior to sample melting, the gaseous contaminants, especially nitrogen and oxygen, remaining in the helium atmosphere were removed by arc melting zirconium metal in the chamber.

The resulting arc-melted bars were somewhat cylindrical in shape with a diameter of approximately 3/8 inch and a length of about 2 inches. These bars were cut into discs 1/4 inch in thickness that served as samples for subsequent heat treatment.

Preparation of alloys richer in tin than Nb_3Sn

All niobium-tin alloys having tin concentrations greater than that of Nb_3Sn were prepared by vacuum annealing techniques. Mixtures of tin with either niobium or Nb_3Sn were placed in closed end quartz tubes and evacuated to a pressure of less than 5 microns of mercury. After several minutes under vacuum, each tube was gently heated to degas its charge. The evacuated tube was then sealed off forming an ampoule containing the metal mixture.

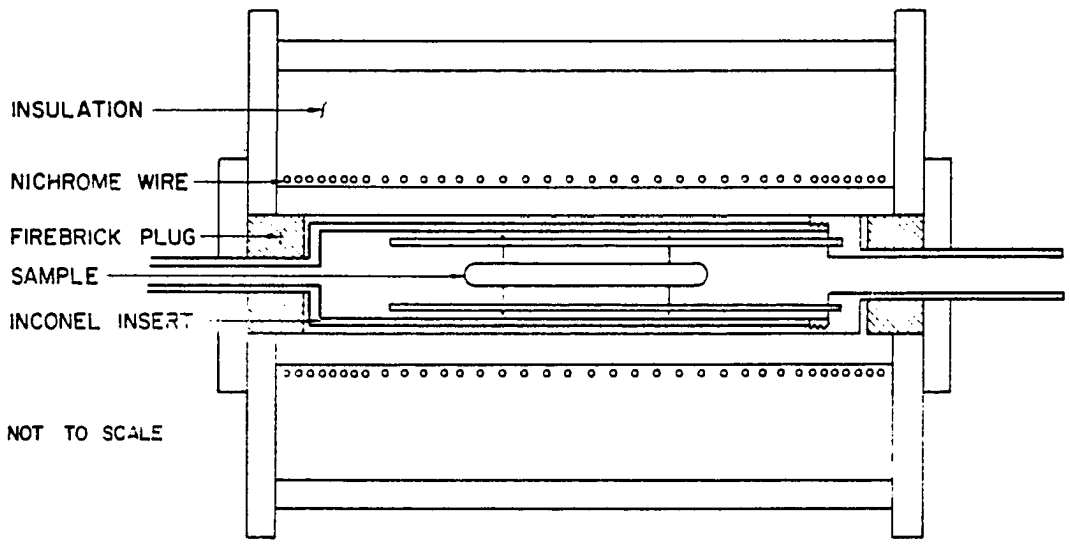
The annealing of the metal mixtures was carried out in a tube type wire wound resistance furnace. A section drawing of the furnace is shown in Figure 2. The furnace was constructed so that the number of windings per unit length near the ends of the 2 inch diameter alundum core was double that for the remainder of the tube. The uneven winding coupled with the inconel insert and firebrick plugs created a nearly uniform temperature zone through most of the length of the furnace. A typical temperature distribution for this furnace assembly is shown in Figure 3.

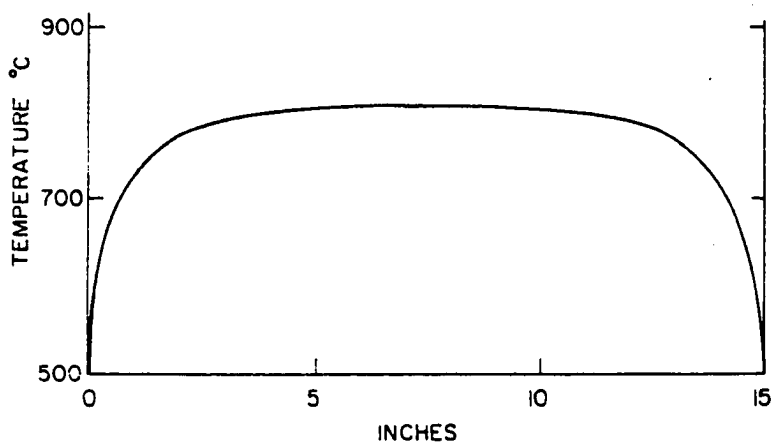
The 1 inch diameter inconel furnace insert contained a sample holder that supported the quartz ampoule within the uniform temperature zone. The ends of the insert tube were fitted with unions so that water hoses could be conveniently attached, thereby permitting water quenching of the samples within the furnace.

The furnace assembly was mounted on a frame that permitted the furnace to be oscillated about a horizontal axis perpendicular to the furnace core. The furnace could be oscillated through approximately 180 degrees (+90 degrees to -90 degrees from the horizontal) at rates up to 50 cycles per minute. The rocking motion of the furnace during equi-

Figure 2. Annealing furnace assembly.

Figure 3. Typical temperature distribution curve for the annealing furnace assembly.


INSULATION
NICHROME WIRE
FIREBRICK PLUG
SAMPLE
INCONEL INSERT
NOT TO SCALE


900
700
500
TEMPERATURE °C
0
5
10
15
INCHES

libration of liquid and semiliquid alloys facilitated rapid homogenization.

Preparation of Nb_3Al

The intermetallic compound Nb_3Al was prepared by aluminothermic reduction of niobium pentoxide (Nb_2O_5) in a bomb according to the reaction:

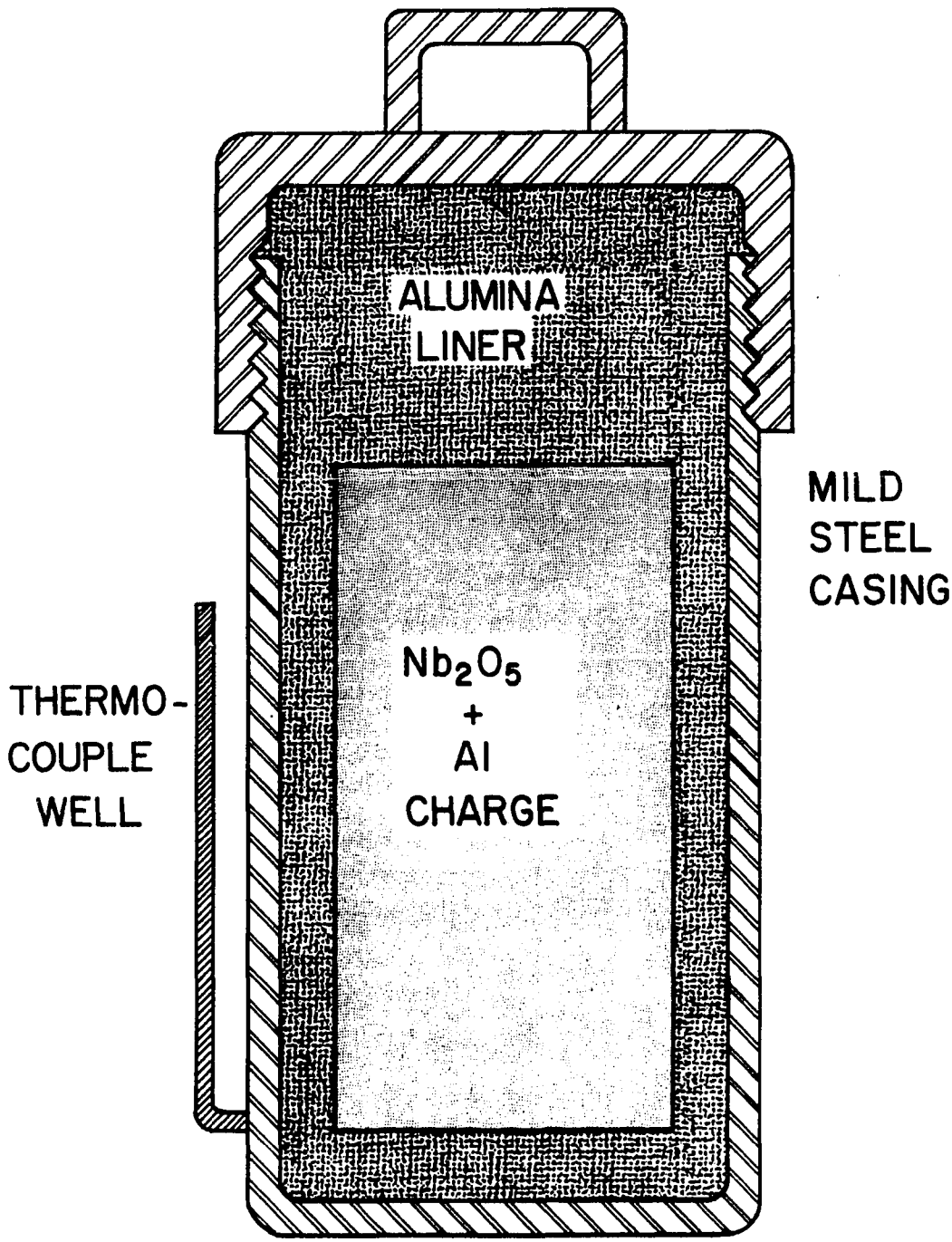
$$3Nb_2O_5 + 12Al \longrightarrow 2Nb_3Al + 5Al_2O_3 \ .$$

The heat released by this reaction was sufficient to melt both products, the niobium-aluminum alloy and the aluminum oxide slag. Preheating the charge to its ignition temperature, however, provided the additional heat that was necessary for a high degree of slag-metal separation.

The reaction was carried out in a 2 1/2 inch diameter steel bomb having a 1/4 inch thick jolt-packed lining of alumina powder. A stoichiometric mixture of niobium pentoxide and aluminum powders according to the above reaction was packed in the lined bomb and covered with more alumina powder. The top of the bomb was then covered with a malleable iron screw cap. A schematic diagram of a packed bomb is shown in Figure 4.

The reaction was initiated by heating the bomb in a gas fired soaking furnace until the charge reached its

Figure 4. Schematic diagram of the aluminothermic reduction bomb.


ALUMINA
LINER
MILD
STEEL
CASING
Nb_2O_5
+
Al
CHARGE
THERMO-
COUPLE
WELL

NOT TO SCALE

ignition temperature. At ignition of the charge, the thermocouple in the well of the side of the bomb was usually at a temperature of 900 to 1000°C. Evidence that the reaction had taken place was shown by a rapid increase in the temperature of the thermocouple. The temperature usually rose an additional 200 to 300 degrees and then began to decrease slowly indicating that the reaction had ceased. The gas to the furnace was then turned off and the bomb left in the furnace until the temperature had dropped back to below the ignition temperature. The bomb was removed from the furnace and air cooled.

Due to the difference in the densities of the liquid metal and slag phases, the metal collected at the bottom of the bomb to form a compact biscuit covered by the slag. The entire contents of the bomb was removed by tapping the inverted steel casing. The metal product was recovered by chipping off the slag. In most instances the slag separated from the metal in one piece.

A chemical analysis of the metal alloy for niobium by the peroxide colorimetric method (11) gave a niobium concentration of 91.1 weight per cent (Nb_3Al is 91.17 weight per cent niobium). X-ray diffraction analysis of this alloy

by the Debye-Scherrer powder method showed it to be simple cubic with a lattice constant of a = 5.184 A. This lattice constant and the intensities of the diffraction lines were in agreement with the data reported by wood, et al. (7) for Nb_3Al. All of the Nb_3Al used in the study of Nb_3Sn-Nb_3Al alloys was prepared in this manner.

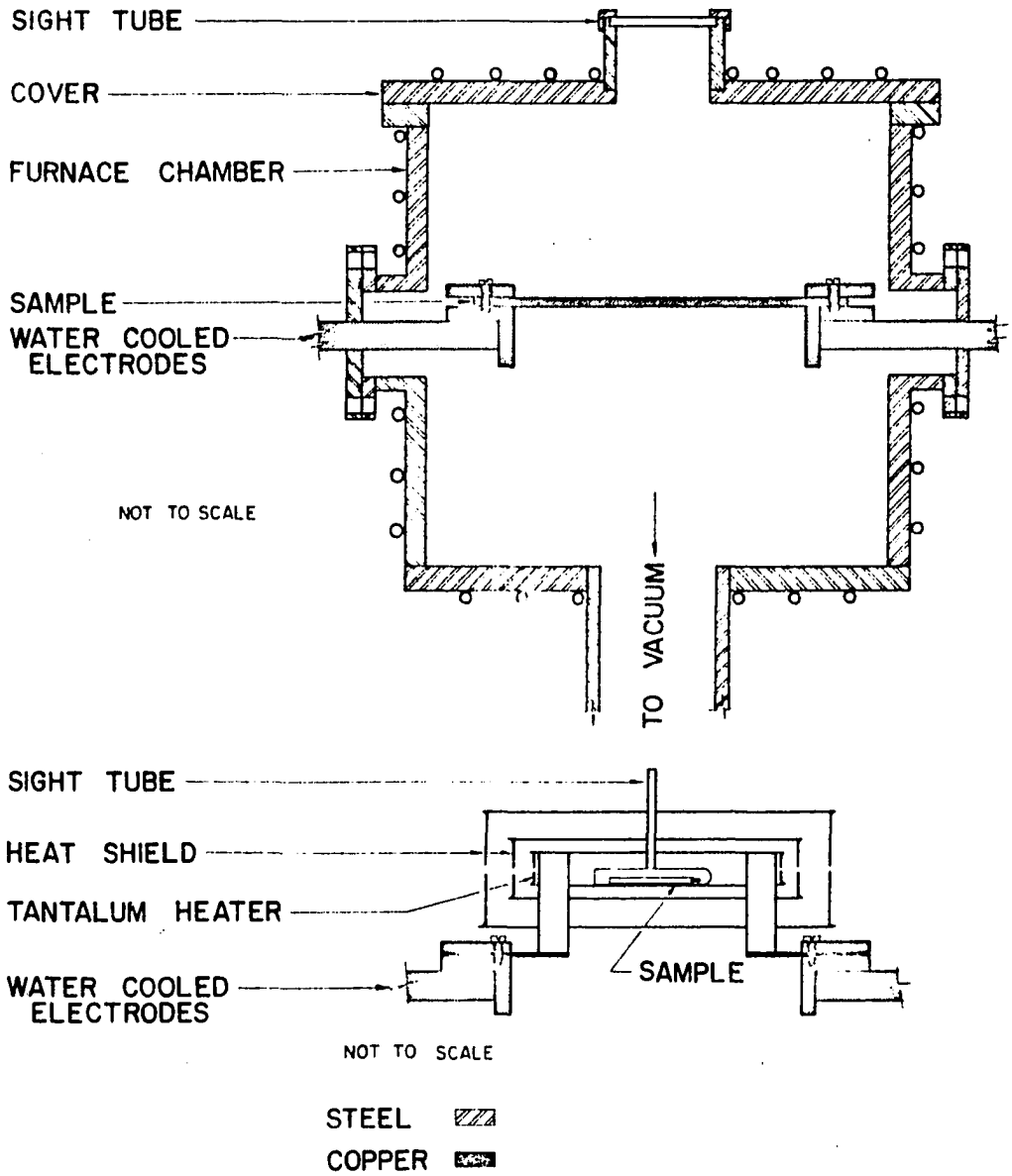
Preparation of Nb_3Sn-Nb_3Al alloys

Specimens of Nb_3Sn-Nb_3Al alloys were prepared by vacuum annealing mixed and compacted powders of the constituents in a vacuum resistance furnace. The materials employed in making the compacts included Nb_3Sn, Nb_3Al, niobium, tin and aluminum. A schematic drawing of the furnace is shown in Figure 5a.

The furnace consisted of two water cooled copper electrodes in a vacuum tight stainless steel cylinder. The bottom of the cylinder was connected through a valve to a vacuum system similar to the one used in the preparation of Nb_3Sn. The top of the cylinder was covered with a stainless steel lid having a Vycor sight glass at its center. The furnace was powered by a 20 kilowatt A.C. power supply. This type of furnace was chosen for annealing Nb_3Sn-Nb_3Al alloys since it was capable of heating them over a much

Figure 5a. Schematic diagram of the vacuum resistance furnace.

Figure 5b. Schematic diagram of the tantalum heating assembly for the vacuum resistance furnace.


SIGHT TUBE
COVER
FURNACE CHAMBER
SAMPLE
WATER COOLED ELECTRODES
NOT TO SCALE
TO VACUUM
SIGHT TUBE
HEAT SHIELD
TANTALUM HEATER
WATER COOLED ELECTRODES
SAMPLE
NOT TO SCALE
STEEL
COPPER

wider range of temperature than the ordinary wire wound resistance furnace.

Annealing the specimens in a vacuum was accomplished in two ways, by direct or by indirect heating. For direct heating, a specimen was mounted between the electrodes and heated by passing the electrical current through it. For indirect heating, a 1/2 inch diameter tantalum tube (see Figure 5b) was mounted between the electrodes. A speciman to be annealed was placed within this tube. The heat was generated by passing electrical current through this tube. The temperatures of the Nb_3Sn-Nb_3Al specimens were monitored by observing its surface with an optical pyrometer.

Phase Equilibria in the Niobium-Tin Alloy System

With the exception of the decomposition temperature of Nb_3Sn, the phase relationships of niobium-tin alloys were determined by studying equilibrated and quenched specimens. Thermal analysis of the alloys by cooling curve techniques was found to be unsatisfactory because of the sluggishness of the transformations.

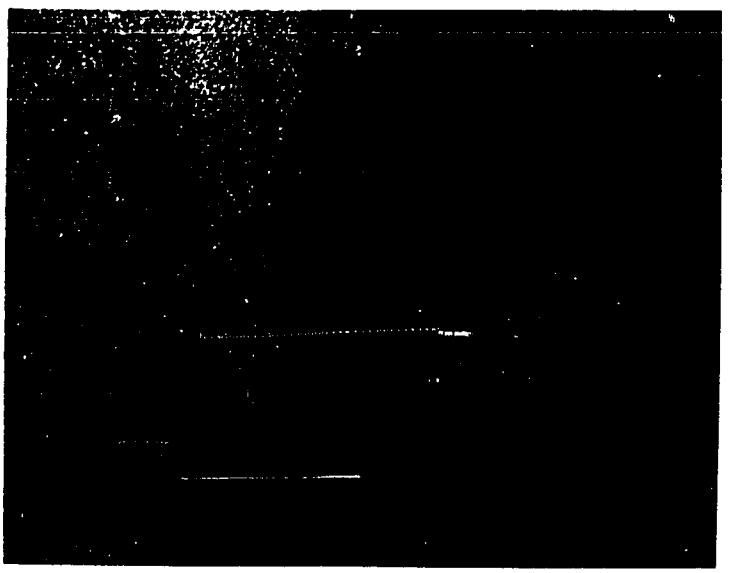
A number of diffusion couples between niobium and tin were prepared at temperatures between 600°C and 1050°C.

Photomicrographs of two of these couples are shown in Figures 6 and 7. The couple shown in Figure 6 was annealed at 1010°C and quenched. Only one phase can be seen between the niobium and tin phases. This phase was assumed to be Nb_3Sn since Mattias, et al. (4) had reported that Nb_3Sn was stable to at least 1200°C. The diffusion couple shown in Figure 7 was annealed at 640°C and quenched. The phase adjacent to the niobium phase was again assumed to be Nb_3Sn. At least one and possibly two additional phases can be seen between the Nb_3Sn and tin phases. When this diffusion couple was observed under polarized light a change in the color of the region between the Nb_3Sn and tin occurred at regular angular intervals as the sample was rotated in the field of the microscope. Since this effect on polarized light occurs only with materials that are non-cubic, the phase or phases so observed could not be Nb_3Sn but had to be new niobium-tin compounds richer in tin than Nb_3Sn. The more tin rich of the compounds was assumed to be $NbSn_2$, analogous to $ZrSn_2$ of the zirconium-tin system and $NbSi_2$ and $NbGe_2$ of the niobium-silicon and niobium-germanium systems, respectively. Early attempts to prepare this compound by annealing mixtures of Nb_3Sn and tin having a

Figure 6. Niobium-tin diffusion couple. Annealed at 1010°C for 170 hrs. Water quenched. Unetched. 250X.

Figure 7. Niobium-tin diffusion couple. Annealed at 640°C for 162 hrs. Water quenched. Unetched. 250X.


Sn
Nb


Sn
Nb

niobium-tin atom ratio of 1:2 gave what appeared to be a one phase alloy. Extensive investigation of the arrangement of the atoms in the unit cell of this compound seemed to substantiate $NbSn_2$ as its stoichiometry. However, later chemical analysis of the residue remaining after leaching this alloy with hydrochloric acid gave a niobium concentration of 37.8 weight per cent. Therefore, this intermetallic compound appears to have a stoichiometry more closely approximating Nb_2Sn_3. Although the stoichiometry of this compound has not been definitely established, it will be referred to as Nb_2Sn_3 in the subsequent discussions.

Another intermetallic compound in the niobium-tin system was identified as a decomposition product of Nb_2Sn_3. A specimen of Nb_2Sn_3 heated to a few degrees above its decomposition temperature was quenched, then leached in hydrochloric acid to remove tin liberated by the decomposition. X-ray analysis by the Debye-Scherrer powder method on the residue remaining after leaching gave a pattern that was different than the patterns of Nb_2Sn_3, Nb_3Sn, niobium, tin or any combination of their patterns. Chemical analysis of the residue gave a niobium concentration of 50.75 weight per cent or a stoichiometry for the compound approximating

Nb_3Sn_2.

Solubility of niobium in tin

The solubility of niobium in liquid tin was determined for five different temperatures from 580°C to 1000°C. Samples containing 4 grams of granular niobium and 10 grams of block tin were sealed in vacuo in quartz ampoules 6 millimeters in diameter and 6 inches in length. A sealed sample was mounted in the furnace (see Figure 2) and annealed for 48 hours at 1000°C. Similar samples annealed at 1000°C for 24 and 72 hours had the same niobium content in their tin phases as the specimen annealed for 48 hours. Therefore, the treatment for 48 hours was more than adequate to establish an equilibrium concentration of niobium in the tin phase at 1000°C.

All other samples to be equilibrated at lower temperatures were first annealed at 1000°C for 48 hours. This preliminary treatment allowed saturation of the liquid tin phase to be attained at lower temperatures through precipitation rather than solution. During most of the equilibration, the furnace was oscillated through approximately 180 degrees at 6 cycles per minute. Six hours prior to quench-

ing, the oscillating motion of the furnace was stopped so that the ampoule was in a vertical position allowing the solid phases which were more dense than the liquid to settle.

Quenching of a specimen was accomplished by passing cold water upwards through the inconel furnace insert. Power to the furnace was turned off and the furnace was allowed to cool. Water flow through the tube was maintained until the furnace had cooled to below the melting point of tin to insure that no particles precipitated during quenching could settle out of the tin phase.

Each sample was broken out of its quartz ampoule and sectioned longitudinally. Microscopic examination of this section after polishing showed that the excess niobium had agglomerated at one end of the specimen as anticipated. Samples of the tin phase were cut from the opposite end of the specimen and analysed for niobium by the peroxide colorimetric method (11). At least three samples from each specimen were analysed. The analyses of the three samples agreed within 20 ppm.

The temperature of equilibration and average niobium content of the tin phase of each specimen are given in Table 5.

Table 5. Solubility of niobium in tin

Annealing treatment	Niobium content of tin phase
48 hours at 1000°C	1980 ppm
48 hours at 1000°C and 59 hours at 900°C	1130 ppm
48 hours at 1000°C and 54 hours at 827°C	830 ppm
48 hours at 1000°C and 56 hours at 744°C	670 ppm
48 hours at 1000°C and 53 hours at 580°C	270 ppm

Solubility of tin in niobium

The limit of solid solubility of tin in niobium between 500°C and 1000°C was determined with metallographic techniques by observing a niobium-tin compound precipitated from supersaturated solid solution alloys. The alloys were prepared from mixtures containing 1, 3, 5 and 10 weight per cent tin, as Nb_3Sn, with niobium in the form of powder compacts that were arc-melted as described previously. Considerable vaporization of the tin occurred during the arc melting so that the tin concentration in the arc-melted bars was less than that originally charged. Chemical analysis of

the "as arc-melted" bars was made using the dithiol colorimetric method (12) for tin. The initial composition of the compacts and the resulting compositions of the four arc-melted alloys are given in Table 6.

Table 6. Compositions before and after arc melting

Composition of the charge before arc melting	Composition of the alloy after arc melting
Nb - 10 w/o Sn	Nb - 3.5 w/o Sn
Nb - 5 w/o Sn	Nb - 2.75 w/o Sn
Nb - 3 w/o Sn	Nb - 0.85 w/o Sn
Nb - 1 w/o Sn	Nb - 0.2 w/o Sn

A sample of each of these alloys was sealed in vacuo in a quartz ampoule, annealed at 1000°C for 48 hours and quenched. Another set of these samples was similarily encapsulated in quartz, annealed at 1000°C for 48 hours followed by a 48 hour anneal at 768°C and water quenched. A third set of samples was similarily sealed, annealed at 1000°C for 48 hours followed by 48 hours at 768°C, then 108 hours at 550°C and water quenched. In order to insure a rapid quench of the specimens the quartz ampoules were

broken just prior to quenching so that the water could be in direct contact with the samples. The quenched specimens were prepared for metallographic inspection by standard polishing techniques and etching with a solution containing, by volume, 10 parts of 48% HF, 5 parts conc. HNO_3, 5 parts conc. H_2SO_4 and 50 parts H_2O.

Photomicrographs of the annealed and quenched alloys are shown in Figures 8 through 17. All specimens contained a fine black precipitate distributed throughout the alloy. This precipitate was believed to be due to the precipitation of Nb_2C and was not related to tin content. The carbon content of the niobium powder used in the preparation of the alloys was high enough to precipitate this carbide.

Figures 8 and 9 show etched niobium-tin alloys containing 3.5 and 2.75 weight per cent tin, respectively, in the "as arc-melted" condition. No precipitation attributable to a niobium-tin compound can be observed. Since the "as arc-melted" samples are essentially quenched from the liquid state, the solubility of tin in niobium must be greater than 3.5 weight per cent at high temperature.

Figures 10 and 11 show the same two compositions as Figures 8 and 9 but annealed at 1000°C and quenched.

Figure 8. Niobium-3.5 w/o tin. As arc melted. Etched. 250X.

Figure 9. Niobium-2.75 w/o tin. As arc melted. Etched. 250X.

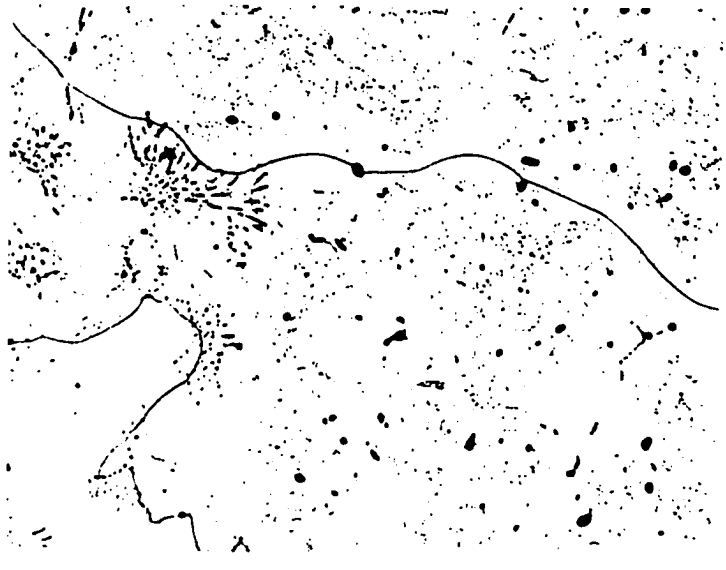


Figure 10. Niobium-3.5 w/o tin. Quenched from 1000°C. Etched. 250X.

Figure 11. Niobium-2.75 w/o tin. Quenched from 1000°C. Etched. 250X.

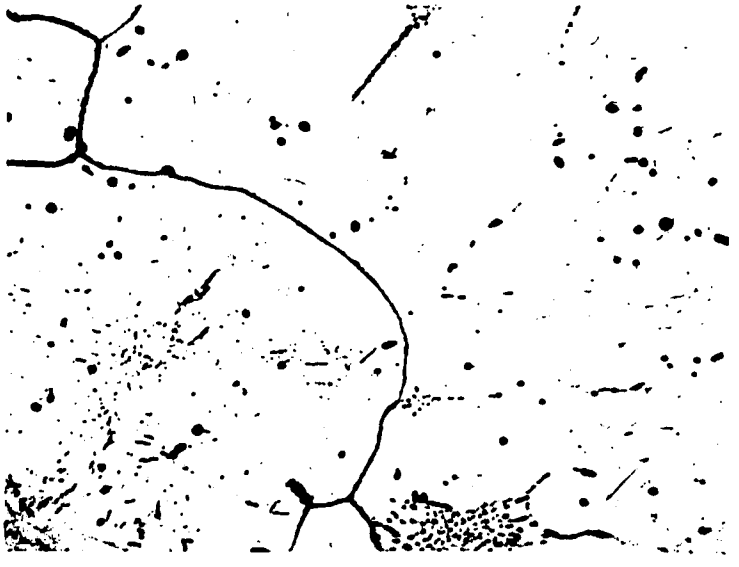


Figure 12. Niobium-3.5 w/o tin. Quenched from 768°C. Etched. 250X.

Figure 13. Niobium-2.75 w/o tin. Quenched from 768°C. Etched. 250X.

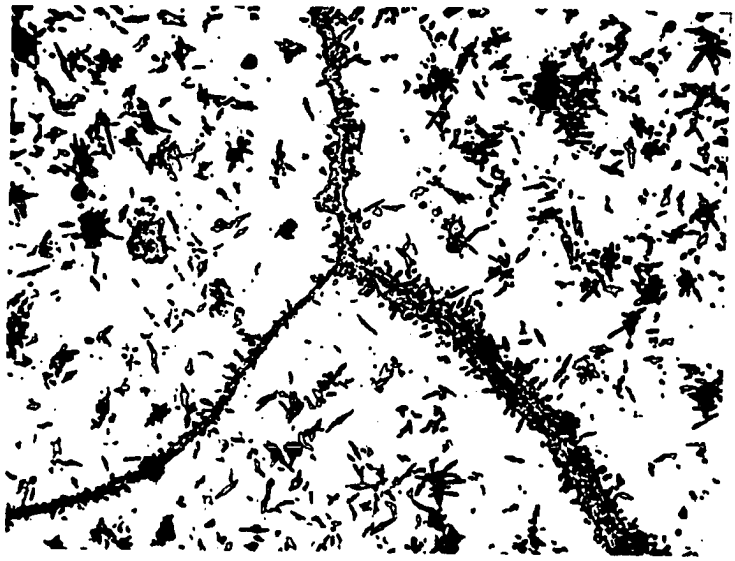
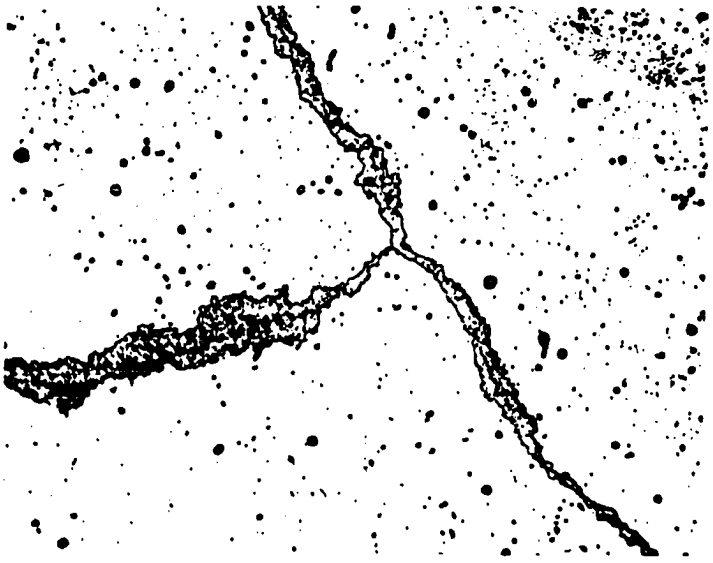


Figure 14. Niobium-3.5 w/o tin. Quenched from 550°C. Etched. 250X.

Figure 15. Niobium-2.75 w/o tin. Quenched from 550°C. Etched. 250X.



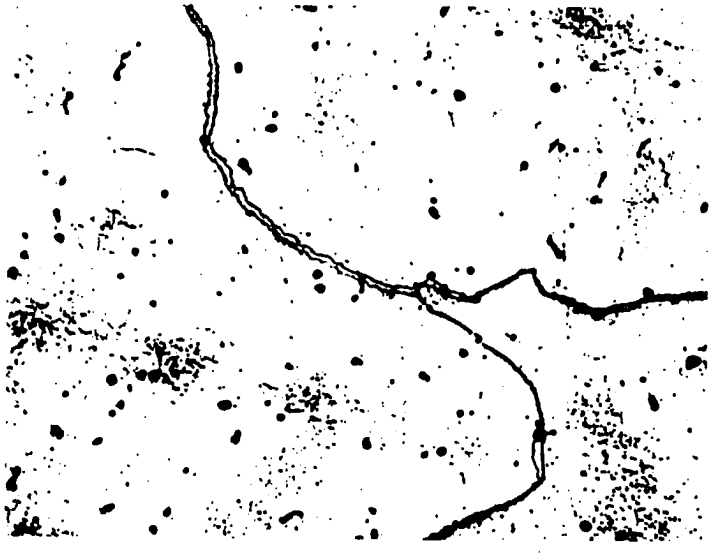
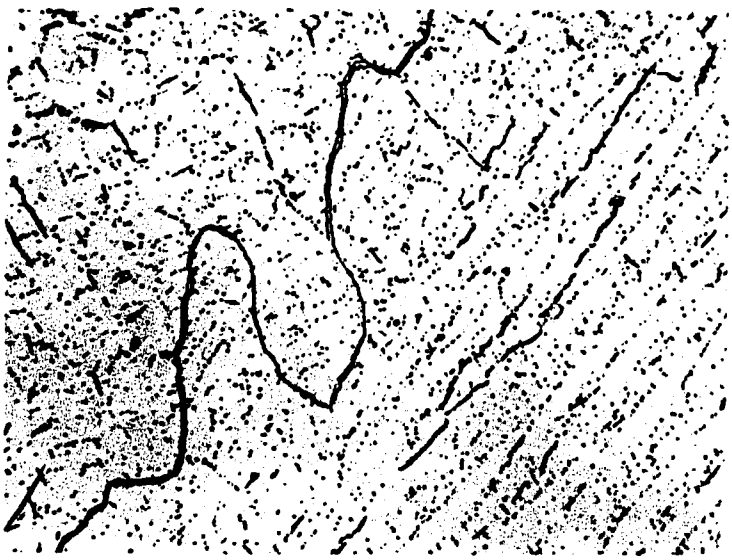


Figure 16. Niobium-0.85 w/o tin. Quenched from 550°C. Etched. 250X.

Figure 17. Niobium-0.2 w/o tin. Quenched from 550°C. Etched. 250X.



Considerable precipitation of a niobium-tin compound, assumed to be Nb_3Sn, can be seen in the 3.5 weight per cent tin alloy but no precipitate of Nb_3Sn can be found in the 2.75 weight per cent tin alloy.

Figures 12 and 13 show the 3.5 and 2.75 weight per cent tin alloys annealed at 768°C and quenched. An increase in the amount of precipitated Nb_3Sn can be observed in the 3.5 weight per cent tin alloy as compared to Figure 10. The precipitate in the grain boundaries of the 2.75 weight per cent tin alloy could be due to either Nb_2C or Nb_3Sn. In any case the amount of this precipitate is so slight that if it were Nb_3Sn, then the solubility limit of tin in niobium at 768°C would be very near to the composition of this alloy.

Figures 14 and 15 show the 3.5 and 2.75 weight per cent tin alloys that had been annealed at 550°C and quenched. Precipitation of Nb_3Sn can be observed in the grain boundaries of both alloys. Therefore, the solubility of tin in niobium at 550°C must be less than 2.75 weight per cent tin.

Figures 16 and 17 are photomicrographs of 0.85 and 0.2 weight per cent tin in niobium alloys that had been annealed at 550°C and quenched. The precipitate that can be seen is due to the Nb_2C. No precipitation attributable to Nb_3Sn

can be observed in either alloy.

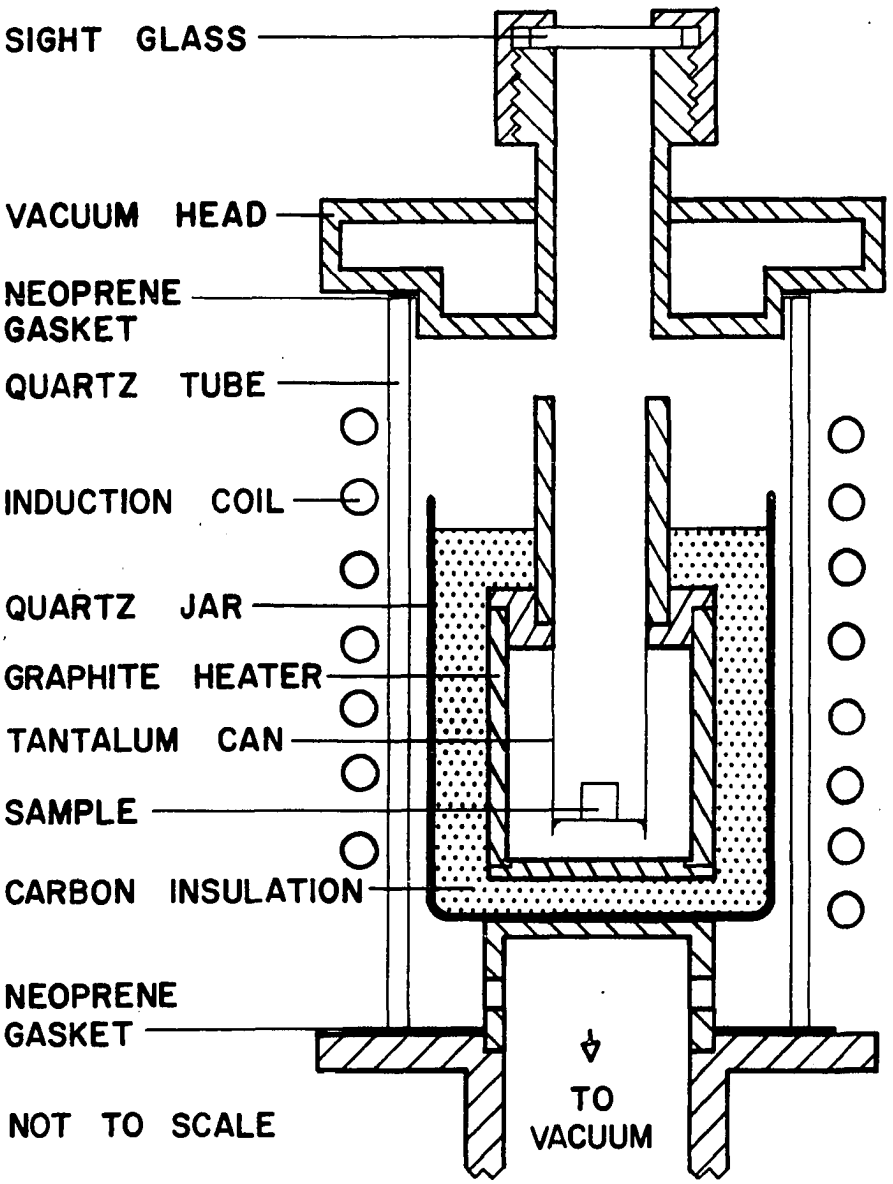
Decomposition of Nb_3Sn

The decomposition of Nb_3Sn was detected by the appearance of a liquid phase during heating of pressed powder compacts of the compound. The temperature at which the decomposition occurred was measured with a disappearing filament optical pyrometer. Compacts having dimensions of 1/4" x 1/4" x 1" were formed by pressing Nb_3Sn powder under 100,000 psi. The "green strength of these compacts was sufficient to permit slicing them into 1/4" cubes without excessive crumbling.

The furnace used to heat these 1/4" cubic specimens to the decomposition temperature was the same as that used for the preparation of Nb_3Sn with slight modification (see Figure 18). The tantalum crucible included here served as the container for the specimens.

After placing a 1/4" cube of pressed Nb_3Sn in the tantalum crucible, the furnace was evacuated to less than 0.1 microns of mercury. The converter was turned on applying 6 KVA to the primary coil. Since the graphite heater contained very little material its temperature and, consequently, the temperature of the Nb_3Sn, rose rapidly. The surface

Figure 18. Vacuum induction furnace used in measurement of Nb_3Sn decomposition temperature.


SIGHT GLASS
VACUUM HEAD
NEOPRENE GASKET
QUARTZ TUBE
INDUCTION COIL
QUARTZ JAR
GRAPHITE HEATER
TANTALUM CAN
SAMPLE
CARBON INSULATION
NEOPRENE GASKET
NOT TO SCALE
TO VACUUM

temperature of the specimen was monitored continuously with the optical pyrometer. The inner tantalum crucible had a depth to diameter of 4:1 which permitted the specimen to be observed at nearly black body conditions. The temperature was recorded when the first liquid appeared on the pressed powder specimen. This temperature was that of the liquid rather than that of the associated solid. However, the difference in the temperature of the liquid and the solid was almost undetectable. This temperature was assumed to be the decomposition temperature of Nb_3Sn. No vaporization of tin could be observed until the liquid appeared and then vaporization was quite evident. The total time from the beginning of the heating to the appearance of liquid on the specimen was 10 minutes.

The results of four such measurements of the decomposition temperature of Nb_3Sn are given in Table 7.

Table 7. Decomposition temperature of Nb_3Sn

Trial Number	Temperature (Corrected for sight glass)
1	2120°C
2	2130°C
3	2130°C
4	2110°C

The sight glass correction was made by observing a standard light source through the optical pyrometer with and without the sight glass interposed. The standard light source was adjusted to the decomposition temperature observed on the above specimens with the sight glass in the optical path. The corrected temperature was then obtained by observing the standard without the sight glass. Since the measurements had been made under nearly black body conditions no other correction of the observed temperature appeared necessary.

Decomposition temperature of Nb_2Sn_3

The decomposition temperature of the compound assumed to be Nb_2Sn_3 was measured by observing the change in microstructure and x-ray powder pattern of niobium-66 w/o tin alloys that had been vacuum annealed at temperatures between 720°C and 860°C and water quenched. This alloy was prepared by heating a mixture of 8 grams of Nb_3Sn and 8.4 grams of tin in an evacuated quartz ampoule at 720° for 350 hours. Samples approximately 1/4 inch in diameter by 1/4 inch thick cut from this alloy were then vacuum annealed at several different temperatures between 720°C and 860°C

and water quenched. The quartz ampoules that contained the samples during annealing were broken just prior to quenching to insure rapid cooling.

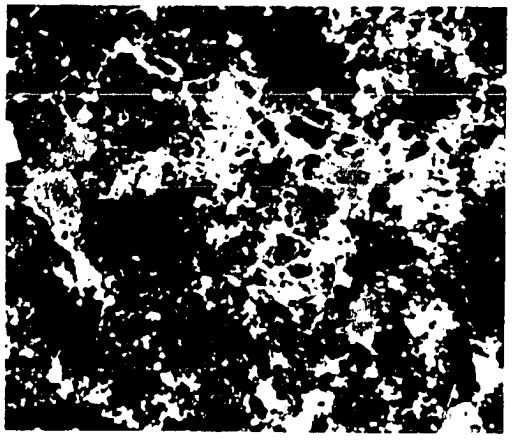
Figures 19a, 19b and 19c show the same area of a niobium-66 w/o tin alloy quenched from 817°C. Figures 19a and 19b show photomicrographs taken under polarized light. Figure 19b was taken after rotating the specimen stage of the metallograph 45 degrees from the orientation of Figure 19a. A change in the color observed for the reflection of polarized light from many grains shows that Nb_2Sn_3 is a non-cubic compound. All specimens of this composition quenched from temperatures between 720°C and 817°C had microstructures that appeared similar to Figures 19a and 19b when observed under polarized light and appeared the same as Figure 19c when observed under bright field illumination.

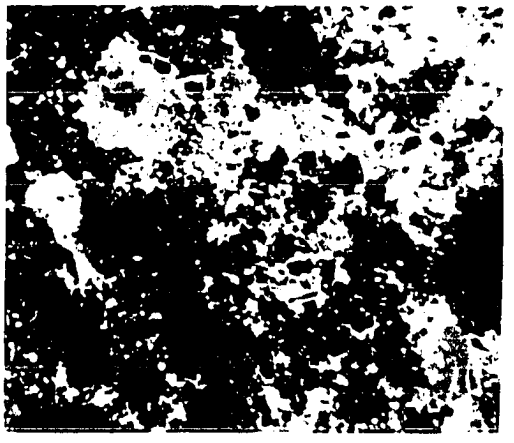
Figures 20a, 20b and 20c show the same area of a niobium-66 w/o tin alloy quenched from 822°C. Figures 20a and 20b show photomicrographs taken under the same conditions as Figures 19a and 19b. Very little change in the color of the grains can be seen. In most cases where any change could be noted, it occurred in the tin matrix rather than in the compound. The lack of radical color change in the

Figure 19a. Nb-66 w/o Sn. Quenched from 817°C. Polarized illumination. Unetched. 250X.

Figure 19b. Nb-66 w/o Sn Quenched from 817°C. Polarized illumination. Unetched. 250X. Rotated 45°.

Figure 19c. Nb-66 w/o Sn. Quenched from 817°C. Bright field illumination. Unetched. 250X. Nb_2Sn_3 with unreacted tin and niobium.





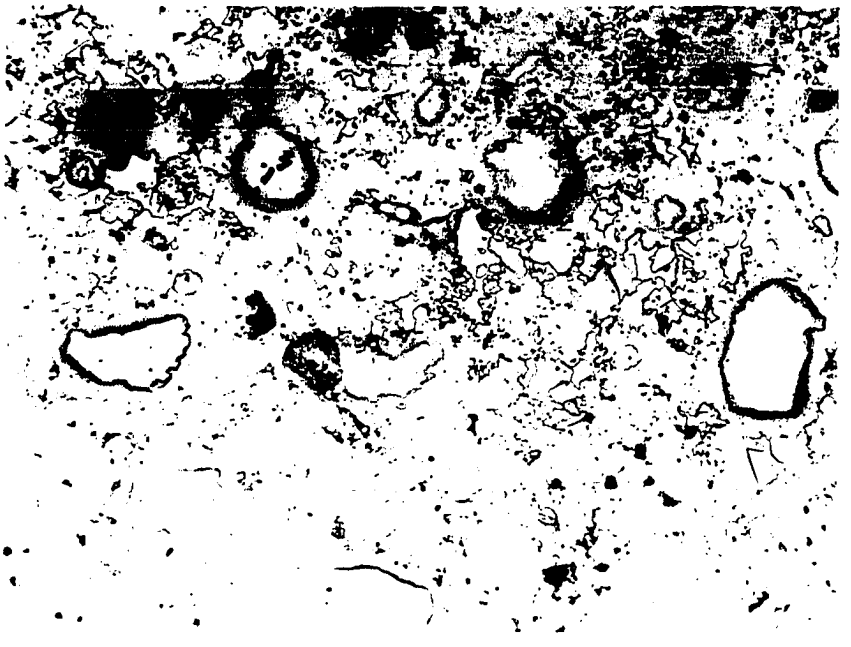
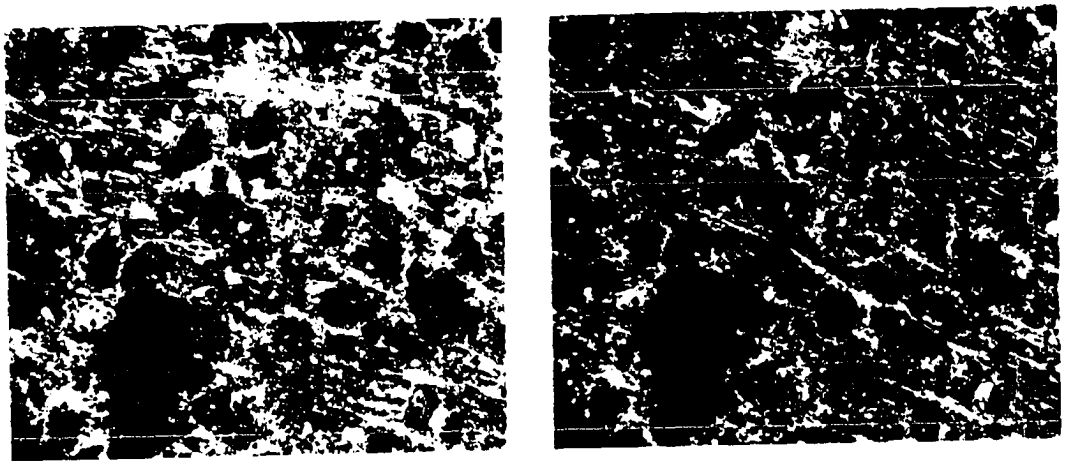
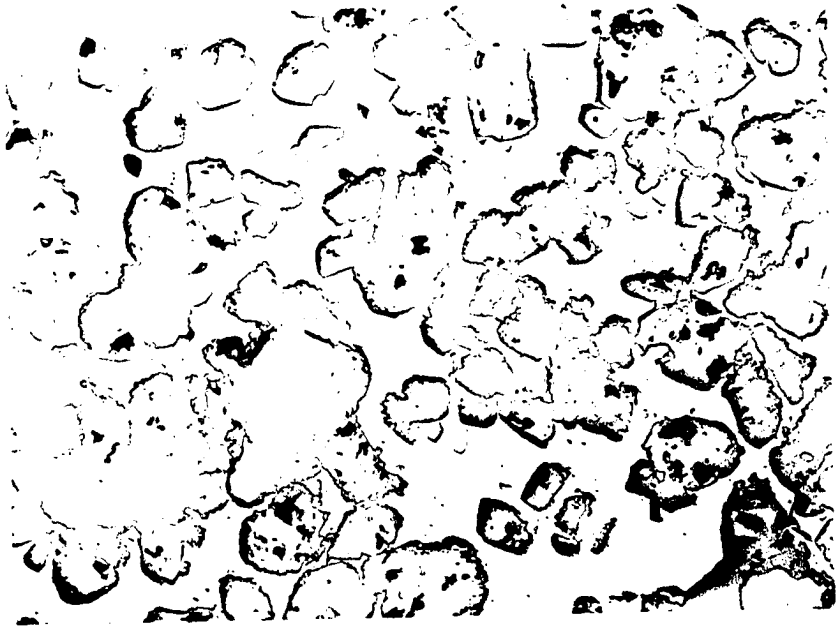


Figure 20a. Nb-66 w/o Sn. Quenched from 822°C. Polarized illumination. Unetched. 250X.

Figure 20b. Nb-66 w/o Sn. Quenched from 822°C. Polarized illumination. Unetched. 250X. Rotated 45°.

Figure 20c. Nb-66 w/o Sn. Quenched from 822°C. Bright field illumination. Unetched. 250X. Nb_3Sn_2 in tin matrix with unreacted niobium.





compound when rotated under polarized light demonstrated that the compound was not Nb_2Sn_3 but was a decomposition product of Nb_2Sn_3. A Debye-Scherrer powder pattern prepared on the residue after leaching this alloy in hydrochloric acid was completely different from that of Nb_2Sn_3. Chemical analysis of the residue gave it an approximate stoichiometry of Nb_3Sn_2.

The niobium-66 w/o tin specimen quenched from 822°C was analysed with a National Research Laboratory Microprobe Analyser. This analysis showed that the matrix surrounding the Nb_3Sn_2 was essentially free of niobium and that the compound had a composition between Nb_2Sn_3 and Nb_3Sn. The Microprobe Analyser also showed that the light grey area included within some of the Nb_3Sn_2 grains (see Figure 20c) was niobium essentially free of tin.

Decomposition of Nb_3Sn_2

Samples of the intermetallic compound Nb_3Sn_2 were prepared for this study by decomposing Nb_2Sn_3 according to the reaction:

$$Nb_2Sn_3 \longrightarrow Nb_3Sn_2 + Sn.$$

A niobium-66 w/o tin alloy was heated in vacuo to 830°C for 2 hours and water quenched. The microstructure of the "as

quenched" alloy was similar to that shown in Figure 20c. The alloy was then leached in hydrochloric acid to remove the uncombined tin. A Debye-Scherrer powder pattern for this leached residue was the same as that obtained from Nb_3Sn_2 remaining after leaching the alloy shown in Figure 20c.

Portions of the leached residue were annealed in vacuo at temperatures between 860°C and 920°C for 2 hours and water quenched. The samples were then leached in hydrochloric acid to remove any tin liberated by the decomposition of Nb_3Sn_2. Debye-Scherrer powder patterns were taken on the residues after four different temperature treatments. A summary of the results obtained from these powder patterns are given in Table 8.

Table 8. Decomposition temperature data for Nb_3Sn_2

Annealing temperature	Debye-Scherrer powder pattern type
860°C	Nb_3Sn_2
900°C	Nb_3Sn_2
910°C	Nb_3Sn_2
920°C	Nb_3Sn

Crystal Structures of Nb_2Sn_3 and Nb_3Sn_2

The investigation of niobium-tin phase equilibria showed that at least two intermetallic compounds in addition to Nb_3Sn were present in the system. Chemical analyses of these two new compounds gave compositions approximating Nb_2Sn_3 and Nb_3Sn_2. Although Debye-Scherrer powder patterns were prepared for each of these compounds, the patterns were found to be too complex for an analysis leading to the determination of their crystal structures. Consequently, single crystal techniques were applied.

Single crystals of Nb_2Sn_3 and Nb_3Sn_2 suitable for crystal structure studies were prepared by vacuum annealing Nb_3Sn in liquid tin. Mixtures of Nb_3Sn powder (-200 mesh) and tin having an overall niobium concentration of 5 weight per cent were sealed in vacuo in quartz tubing. One of the samples was mounted in the annealing furnace (see Figure 2), annealed at 1000°C for 24 hours followed by 168 hours at 780°C to form Nb_2Sn_3. After annealing, the alloy was furnace cooled to room temperature. The furnace was oscillated through approximately 180 degrees during the entire annealing and cooling operation so as to reduce the agglomeration of the crystals.

Nb_3Sn_2 single crystals were prepared in another sample in the same manner as above except that the final annealing temperature was 880°C and the alloy was quenched to room temperature. After the heat treatments, each alloy was leached with hydrochloric acid to remove the unreacted tin.

The residue of each alloy contained many well shaped single crystals of its respective compound. Most of the crystals of Nb_2Sn_3 were hexagonal-shaped platelets similar to those found during the preparation of Nb_3Sn (see page 22). A representative crystal was selected, mounted on a glass fiber and aligned in a goniometer head so that the rotation axis of the crystal in a Weissenberg camera was parallel to the large, flat faces of the platelet. Most of the crystals of Nb_3Sn_2 were right parallelepipeds with adjacent sides of unequal length. A representative crystal was selected, mounted on a glass fiber and aligned in a goniometer head so that the rotation axis of the crystal in a Weissenberg camera was parallel to the longest edges of the crystal.

Diffraction symmetry and systematic extinctions of diffraction maxima for both compounds were determined from Weissenberg and precession photographs (13). A set of six Weissenberg layer photographs, h0ℓ, h1ℓ, $\cdots$, h5ℓ, for each

compound using copper Kα radiation. Two sets of precession photographs, 0kℓ, 1kℓ, $\cdots$, 3kℓ and hk0, hk1,$\cdots$, hk8, were prepared for each compound using molybdenum Kα radiation.

In every case $C_2\ell$ reciprocal lattice symmetry was observed. The three axes of each compound as seen on the Weissenberg and precession photographs were mutually perpendicular and of unequal lengths. These conditions indicate that both Nb_2Sn_3 and Nb_3Sn_2 have orthorhombic crystal structures. The Weissenberg and precession photographs were indexed and the positions of the reflections having Miller indices of h00, 0k0, and 00ℓ were measured for each of the compounds. The measurements were converted to their corresponding Bragg angles and approximate lattice constants calculated. Results of these calculations for the two compounds are listed in Table 9.

Table 9. Approximate lattice constants for Nb_2Sn_3 and Nb_3Sn_2 calculated from Weissenberg and precession data

Crystal axis	Approximate lattice constants	
	Nb_2Sn_3	Nb_3Sn_2
a	5.7 A	5.6 A
b	9.7 A	9.3 A
c	18.8 A	16.8 A

The systematic extinction conditions for both Nb_2Sn_3 and Nb_3Sn_2 are listed in Table 10. Interpretation of the extinctions for Nb_2Sn_3 resulted in the determination of one unique space group, D_{2h}^{24} - Fddd, for this compound. Interpretation of the extinctions for Nb_3Sn_2 resulted in limiting the possible space groups for this compound to four, C_{2v}^{20} - Imm, D_2^8 - I222, D_2^9 - $I2_i2_i2_i$ or D_{2h}^{25} - Immm.

More precise lattice constants for each crystal were determined from back-reflection Weissenberg photographs (14) taken with copper Kα radiation. One photograph for each compound was taken such that h0ℓ data were obtained. The crystals were then remounted such that 0kℓ data were obtained. This permitted all three lattice constants for each crystal to be determined simultaneously from back-reflection data.

The lattice constants of the two compounds were calculated on an IBM 704 computer using the computer program written by Mueller and Heaton (15). The data were given a weighting factor (w), where $w = f(1/\sin^2 2\theta)$ with θ being the Bragg angle, and were extrapolated against the Nelson-Riley function (16). Results of the calculation of more precise values for the lattice constants of Nb_2Sn_3 and

Table 10. Systematic extinction of diffraction maxima for Nb_2Sn_3 and Nb_3Sn_2

Class of Reflection	Nb_2Sn_3		Nb_3Sn_2	
	Extinction Condition	Symbol of Symmetry Element	Extinction Condition	Symbol of Symmetry Element
hkℓ	h+k ≠2n h+ ℓ ≠2n k+ℓ ≠2n	F	h+k+ℓ ≠2n	I
0kℓ	k+ℓ ≠4n	d	k+ℓ ≠2n	*
h0ℓ	h+ ℓ ≠4n	d	h+ ℓ ≠2n	*
hk0	h+k ≠4n	d	h+k ≠2n	*
hhℓ	h ≠2n	*	ℓ ≠2n	*
h00	h ≠4n	*	h ≠2n	*
0k0	k ≠4n	*	k ≠2n	*
00ℓ	ℓ ≠4n	*	ℓ ≠2n	*
hh0	h ≠2n	*	no data	*

*redundant.

Nb_3Sn_2 are listed in Table 11.

Table 11. Lattice constants for Nb_2Sn_3 and Nb_3Sn_2 calculated from back-reflection Weissenberg data

Crystal axis	Lattice constants*	
	Nb_2Sn_3	Nb_3Sn_2
a	5.72 ± 0.04 A	5.637 ± 0.001 A
b	10.03 ± 0.06 A	9.204 ± 0.003 A
c	19.01 ± 0.06 A	16.677 ± 0.003 A

*50% confidence.

Nb_3Sn-Nb_3Al Alloy Studies

Preparation of Nb_3Sn-Nb_3Al alloys

Three methods of preparing Nb_3Sn-Nb_3Al alloys were employed. One method was suggested by the report of Olsen, et al. (17) who prepared long lengths (up to 8000 feet) of a composite wire which had a core of Nb_3Sn and a jacket of niobium. They filled niobium tubing with cylindrical compacts of mixed niobium and tin powders, closed the ends of the tube with nickel plugs and reduced this composite to 0.032 inch diameter wire by swaging and drawing. After drawing, they annealed the wire at 1000°C for 16 hours to

convert the niobium and tin into Nb_3Sn. A method similar to that of Olsen, et al. was used to prepare some of the samples for the investigation of Nb_3Sn-Nb_3Al alloys. Niobium, tin and aluminum powders were mixed and packed in niobium tubes that were 3/8 OD x 1/4" ID x 1 1/4" long. The tubes were sealed under helium by welding 1/4" diam. x 1/16" thick niobium caps on the ends. The tubes were then swaged to 1/4" OD specimens.

The swaaed specimens were annealed at 1000°C in vacuo for 72 hours in the furnace shown in Figure 5a to allow the niobium-tin-aluminum charge to react to form the Nb_3Sn-Nb_3Al alloys. The amount of tin and aluminum in each specimen was determined on the basis of reaction with only the niobium that was added as powder. No attempt was made to compensate for the tin and aluminum that might react with the wall of the niobium tube. The samples prepared in this manner are hereafter referred to as "swaged" Nb_3Sn-Nb_3Al alloys.

Another set of Nb_3Sn-Nb_3Al alloys was prepared by packing mixed Nb_3Sn and Nb_3Al powders in tantalum tubes 1/4" diam. x 1 1/2" long. The ends of the tubes were then crimped and the tubes then rolled to 1 millimeter square cross section wires. Alloying of the Nb_3Sn and Nb_3Al into

Nb_3Sn-Nb_3Al alloys was accomplished by annealing the rolled wires in the vacuum furnace (see Figure 5a) for 1 hour at 1500°C. These samples are hereafter referred to as "rolled" Nb_3Sn-Nb_3Al alloys.

A third set of alloys was prepared by sintering powder mixtures of Nb_3Sn and Nb_3Al that had been pressed into 1/4" x 1/4" x 2" compacts under 80,000 psi. A small amount of stearic acid was added to the powder before mixing to act as a binder and improve the "green" strength of the compacts. These compacts were then sintered in the heater assembly shown in Figure 5b.

In order to evaporate the stearic acid binder, the compacts were heated to 300°C in vacuo and held at that temperature until the pressure within the furnace dropped to less than 0.005 microns. The compacts were then heated to 1250°C and annealed in vacuo for 8 hours. The sintered compacts were cooled to room temperature in steps of approximately 200°; the specimens were annealed for 1/2 hour at one temperature before cooling to the next. These samples are hereafter referred to as "pressed" Nb_3Sn-Nb_3Al alloys.

Zero field superconducting transformation temperature of Nb_3Sn-Nb_3Al alloys

Certain materials exhibit a behavior at low temperatures which is referred to as superconductivity and is considered to be associated with frictionless motion of the electrons of the material. A phase of the behavior of these materials, called superconductors, is the tendency for the interior of the material to be screened from external magnetic fields and as a result the magnetic induction within massive material tends to vanish. This effect is considered to be caused by frictionless surface currents (18). The transformation of a material from the normal to the superconducting state depends upon both the temperature and the magnetic field applied to it. Consequently, the transition must be expressed in terms of both temperature and magnetic field.

In theory, the transition from the normal to the superconducting state is an instantaneous reversible reaction. On cooling through the transformation temperature associated with the applied magnetic field, the resistance of the material to electrical current should immediately drop to zero. Due to the reversibility of this effect one should be able to measure the transformation temperature by

observing the abrupt change in the resistance to or from zero on cooling or heating, respectively.

For this investigation, a technique utilizing the principle discussed above was used to determine the superconducting transformation temperatures of Nb_3Sn-Nb_3Al alloys in the absence of an intentionally applied magnetic field. In the experiments, the voltage drop across the sample was observed directly. A specimen of an Nb_3Sn-Nb_3Al alloy was immersed in the cryostat described by Colvin, et al. (19) and the voltage drop for the alloy was measured at temperatures between $4.2^{o}K$ and $20^{o}K$ by the four probe method with current reversal. A continuously monitored current of 100 milliamps supplied by a 6 volt battery was used to develop a measurable voltage drop across the specimen in its normal conducting state. The specimen temperature was monitored with a calibrated copper-constantan thermocouple.

A plot of voltage drop versus temperature was constructed for each of the Nb_3Sn-Nb_3Al alloys measured in the manner described above. The transformation of each alloy from the normal to the superconducting state did not occur at a single unique temperature but rather over a range of temperatures. For this reason, it was not possible to arrive at

a single transformation temperature for any alloy. Consequently, three points were taken to represent the plot of voltage versus temperature for each alloy; 1. the temperature at which the transformation from superconducting to normal behavior began, 2. the temperature of the midpoint of the transformation, and 3. the temperature at which the transformation ended. Plots of these points versus composition for the "swaged" and for the "pressed" Nb_3Sn-Nb_3Al alloys are given in Figures 21 and 22.

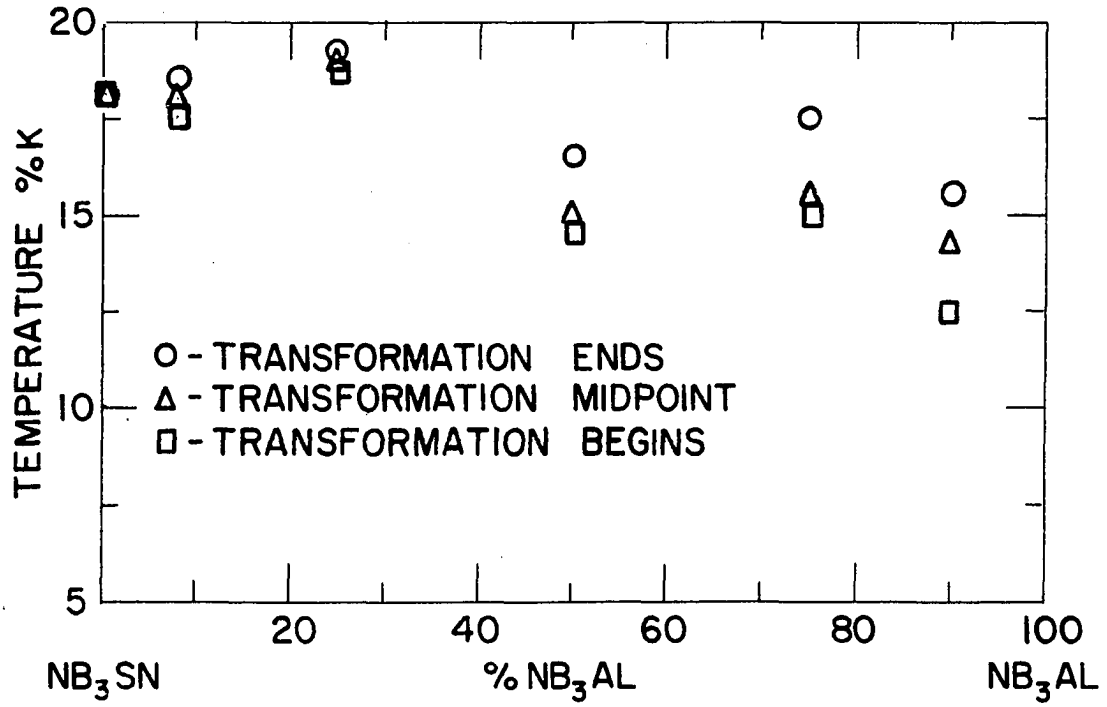
Crystallography of Nb_3Sn-Nb_3Al alloys

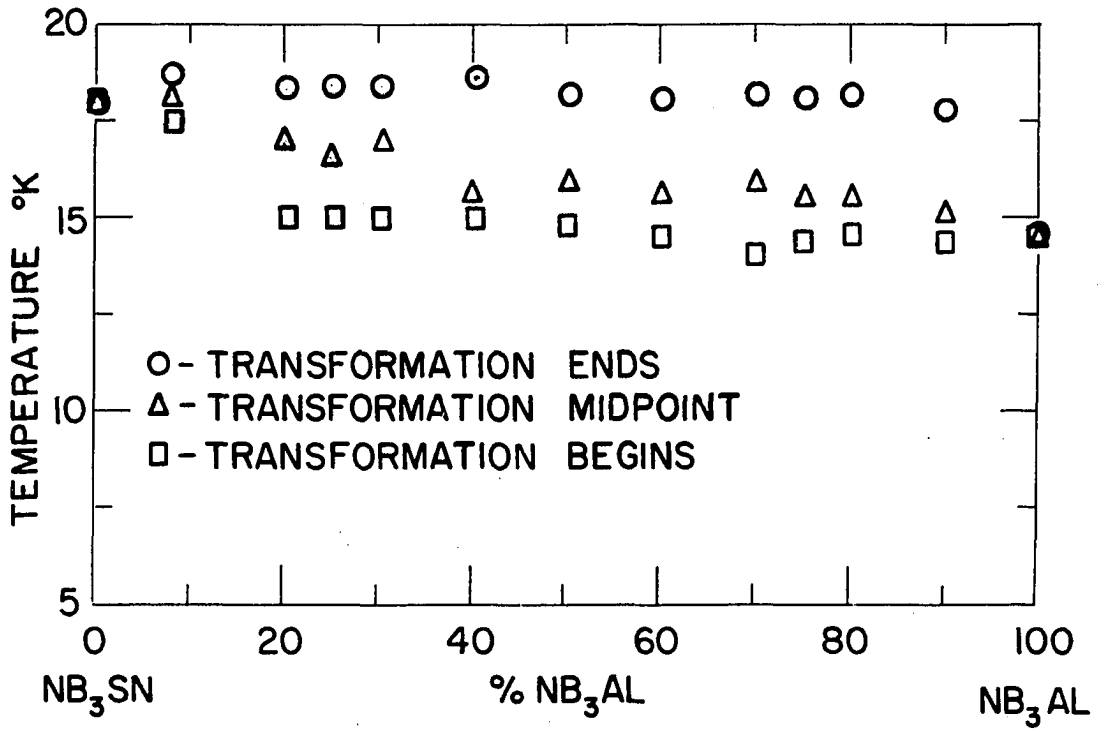
The variation of lattice constants of the Nb_3Sn-Nb_3Al alloys with composition was studied using Debye-Scherrer powder techniques. The samples for the x-ray analyses were obtained from the "rolled" alloys. A short section was selected from the center of each wire, separated from its tantalum jacket and crushed into -200 mesh powder. The diffraction patterns of these powders were prepared in a 114.7 millimeter diameter Debye-Scherrer camera using copper $K\alpha$ radiation. All lines in the diffraction pattern of each alloy could be accounted for by a single phase simple cubic structure.

The lattice constant for each alloy was calculated from

Figure 21. Zero field superconducting transformation temperatures versus composition for the "swaged" Nb_3Sn-Nb_3Al alloys.

Figure 22. Zero field superconducting transformation temperatures versus composition for the "pressed" Nb_3Sn-Nb_3Al alloys.


20
15
10
5
TEMPERATURE °K
O - TRANSFORMATION ENDS
Δ - TRANSFORMATION MIDPOINT
□ - TRANSFORMATION BEGINS
20
40
60
80
100
NB3SN
% NB3AL
NB3AL


20
15
10
5
TEMPERATURE °K
O - TRANSFORMATION ENDS
Δ - TRANSFORMATION MIDPOINT
□ - TRANSFORMATION BEGINS
0
20
40
60
80
100
NB3SN
% NB3AL
NB3AL

the data occurring in the back-reflection region of the diffraction pattern, that is, from those reflections having Bragg angles between 45 and 90 degrees. The calculations were performed on an IBM 704 computer using the program written by Mueller and Heaton (15). The calculations employed a weighting factor (w), where $w = f(1/\sin^2 2\theta)$ with θ being the Bragg angle, and the Nelson-Riley function to give extrapolated values of the lattice constants. The results of these calculations for the Nb_3Sn-Nb_3Al alloys are listed in Table 12.

Table 12. Lattice constants of Nb_3Sn-Nb_3Al alloys

Mole per cent Nb_3Al in alloy	Lattice constant*
10%	5.2856 ± 0.0001 A
20%	5.2811 ± 0.0001 A
25%	5.2801 ± 0.0001 A
30%	5.2680 ± 0.0001 A
40%	5.2539 ± 0.0001 A
50%	5.2435 ± 0.0001 A
60%	5.2378 ± 0.0001 A
70%	5.2236 ± 0.0004 A
75%	5.228 ± 0.004 A
80%	5.2091 ± 0.0001 A
90%	5.1967 ± 0.0001 A

*95% confidence.

DISCUSSION OF RESULTS

Niobium-Tin Alloys

The equilibrium data obtained for the niobium-tin binary alloy system was sufficient to permit a general understanding of the temperature-composition phase relationships for these alloys. Considerable disagreement exists between the results found in this investigation and that reported in the literature on this alloy system. The major features of the system according to the results obtained in this investigation are discussed in some detail. A proposed constitutional diagram for niobium-tin alloys based on these results is presented in Figure 23.

The solubility of tin in niobium (see Figure 24) was much lower than anticipated from analogous systems and the Hume-Rothery size criterion. It varied from approximately 2.5 weight per cent tin at 550°C to approximately 3 weight per cent tin at 1000°C. These solubility limits were less than one-third those reported by Agafonova, et al. (6) over a similar temperature range. Since the "as arc melted" samples (see Figures 8 and 9) showed no niobium-tin precipitate, the solubility of tin in niobium evidently continues

Figure 23. Proposed niobium-tin binary constitution diagram.

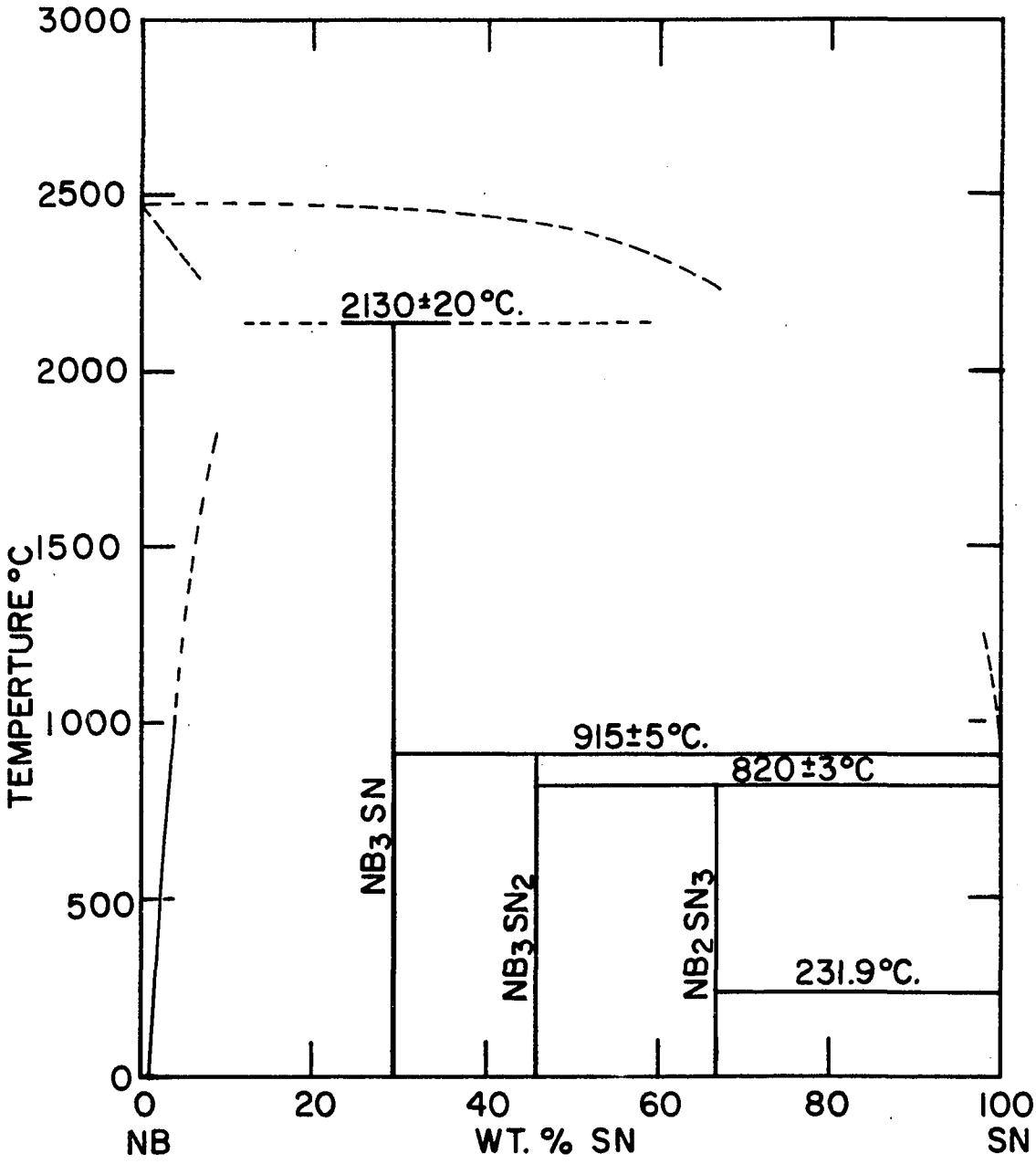
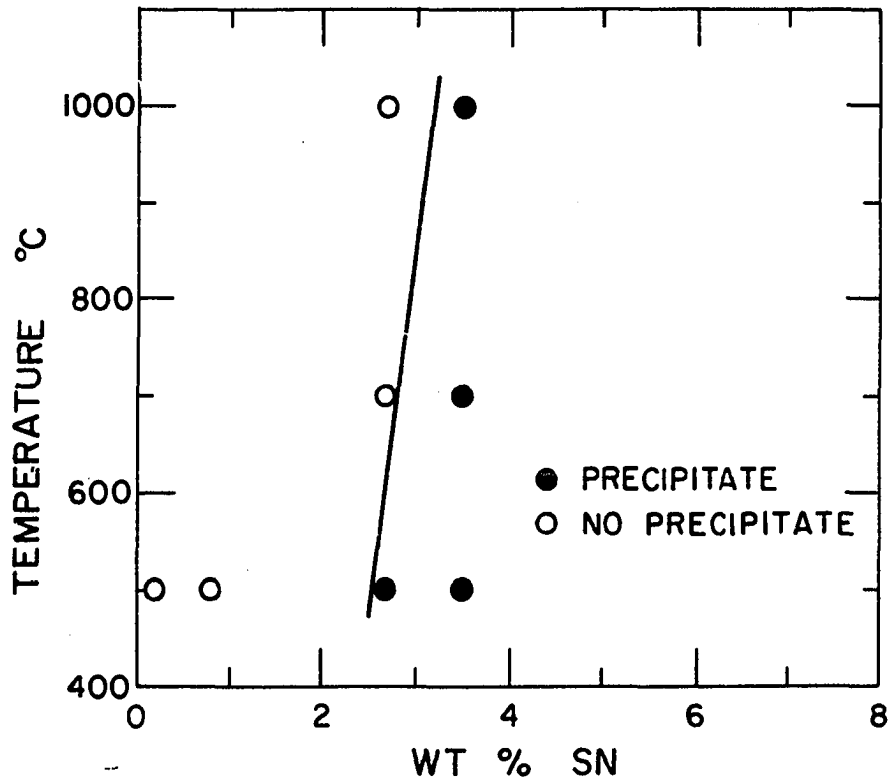
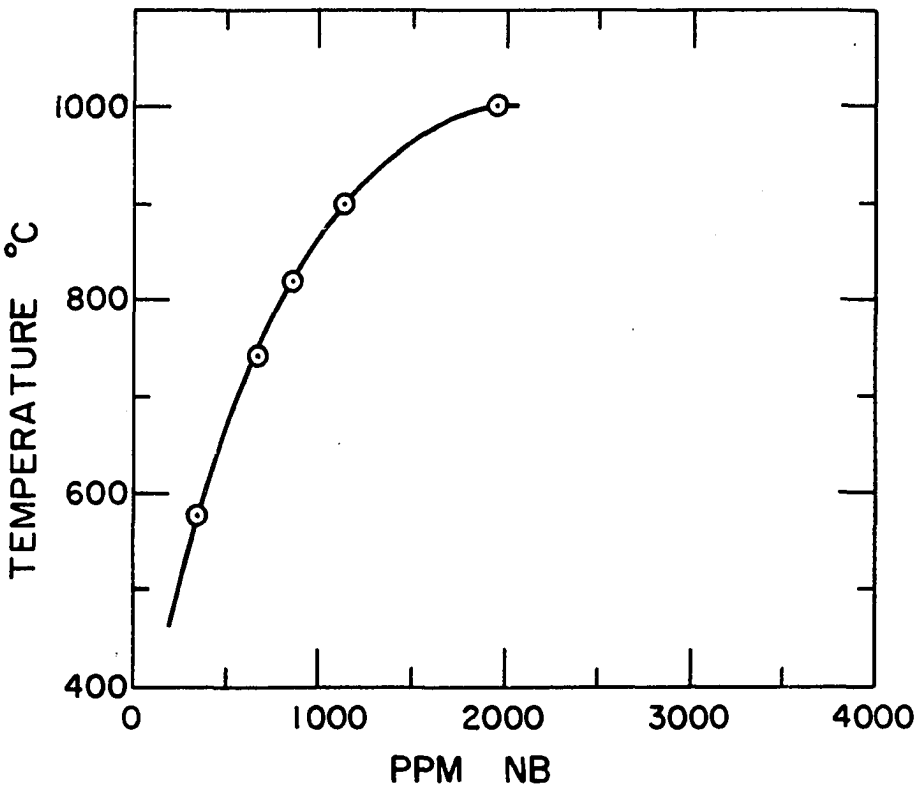

3000
2500
2000
1500
1000
500
0
TEMPERTURE °C
2130±20°C.
915±5°C.
820±3°C
231.9°C.
NB3SN
NB3SN2
NB2SN3
0
20
40
60
80
100
NB
WT. % SN
SN

Figure 24. Solubility of tin in niobium.

Figure 25. Solubility of niobium in molten tin.


TEMPERATURE °C
1000
800
600
400
0
2
4
6
8
WT % SN
PRECIPITATE
NO PRECIPITATE


TEMPERATURE °C
1000
800
600
400
0
1000
2000
3000
4000
PPM NB

to increase with temperature. However, it is doubtful that the maximum solubility approaches the 14 weight per cent tin reported in the reference cited (6).

The solubility of niobium in liquid tin was low, as anticipated from analogous alloy systems. It varied from 270 ± 20 ppm at 580°C to 1980 ± 20 ppm at 1000°C. However, when the data are extrapolated to temperatures above 1000°C, the solubility of niobium in liquid tin appears to increase quite rapidly (see Figure 25).

In contrast to the results of Agafonova et al., two intermetallic compounds in addition to Nb_3Sn were found to exist in the niobium-tin system. These two new compounds appear to have stoichiometries of Nb_2Sn_3 and Nb_3Sn_2. Nb_2Sn_3, on heating, decomposed peritectically into Nb_3Sn_2 and liquid tin at 820 ± 3°C. The compound Nb_3Sn_2, on heating, decomposed by peritectic reaction into Nb_3Sn and liquid tin at 915 ± 5°C.

The peritectic temperature of Nb_3Sn, as measured with an optical pyrometer, was found to be at 2125 ± 25°C. This temperature was in fair agreement with the 2000 ± 25°C reported by Agafonova and coworkers. Although the reproducibility of the data suggests a smaller error in the measure-

ment of the decomposition temperature, the accuracy of the method of measurement was such that an estimate of $\pm$ 25 centigrade degrees seemed more appropriate. Unfortunately, no convenient method for exact determination of the degree of accuracy was found so that this estimate was based entirely on past experience with similar measuring equipment.

Both of the new intermetallic compounds found in the niobium-tin system had orthorhombic crystal structures. An analysis of the systematic extinction of diffraction maxima for Nb_2Sn_3 resulted in the determination of one unique space group, D_{2h}^{24} - Fddd, for this compound. The systematic extinction data from Nb_3Sn_2 could not be analysed to a unique space group. The symmetry of this compound was such that the data obtained limited the number of possible space groups to four, D_2^8 - I222, D_2^9 - $I2_i2_i2_i$, D_{2h}^{25} - Immm and C_{2v}^{20} - Imm. In order to determine which of the four is the unique space group for Nb_3Sn_2, additional diffraction intensity data is required.

Although the most tin rich compound in the niobium-tin alloy system has been referred to as Nb_2Sn_3 throughout this report, this stoichiometry has not yet been definitely established. At the beginning of the investigation of the

crystal structure of this compound its stoichiometry was thought to be "$NbSn_2$", analogous to $ZrSn_2$. This analogy seemed even more reasonable when it was found that "$NbSn_2$" had a D_{2h}^{24} - Fddd space group, which was the same as that for $ZrSn_2$. However, efforts to locate the atoms in the "$NbSn_2$" unit cell based on the known positions of the atoms in $ZrSn_2$ (20) failed completely giving the first evidence that a complete analogy was not possible.

The intermetallic compound $CuMg_2$ (20) has the same structure, D_{2h}^{24} - Fddd, and also has lattice parameters closely approximating those of "$NbSn_2$". An attempt to locate the atom positions in "$NbSn_2$" based on those in $CuMg_2$ resulted in a partial refinement of the data, but the refinement was not sufficient to definitely establish the atom positions.

At this point in the investigation new bulk specimens of the most tin rich compound were prepared with great care to insure that no other phases were present. Chemical analysis of these specimens revealed that the compound had a niobium concentration of 37.8 weight per cent, or a stoichiometry approximating Nb_2Sn_3.

A calculation of the number of atoms per unit cell

based on the measured lattice constants of this compound and the average volume for the niobium atom in metallic niobium and the tin atoms in alpha-tin for either stoichiometry resulted in the determination that the unit cell should contain a total of approximately 40 atoms. If the stoichiometry were $NbSn_2$, then the number of atoms per unit cell for a D_{2h}^{24} - Fddd space group would have to be 24 or some multiple of 24. The most reasonable number of atoms per unit cell based on $NbSn_2$, therefore, would be 48. If the compound were Nb_2Sn_3, then the number of atoms per unit cell would have to be 40 or some multiple of 40. Therefore, a unit cell based on Nb_2Sn_3 as the stoichiometry containing 16 niobium atoms and 24 tin atoms, or a total of 40 atoms per unit cell, appeared to be highly compatible with the number of atoms calculated, 40, from the volume of the unit cell. However, if the volume of the tin atoms is based on that calculated from beta-tin, then the number of atoms per unit cell for the niobium-tin compound is approximately 46. Therefore, a unit cell based on $NbSn_2$ containing 16 atoms of niobium and 32 atoms of tin, or a total of 48 atoms per unit cell also appears to be a possible arrangement.

Since the chemical analysis of the most tin-rich

niobium-tin compound indicates Nb_2Sn_3 this stoichiometry has been assumed even though there was evidence to support $NbSn_2$. The arrangement of the atoms in the unit cell is probably quite closely related to that in $CuMg_2$.

Nb_3Sn-Nb_3Al Alloys

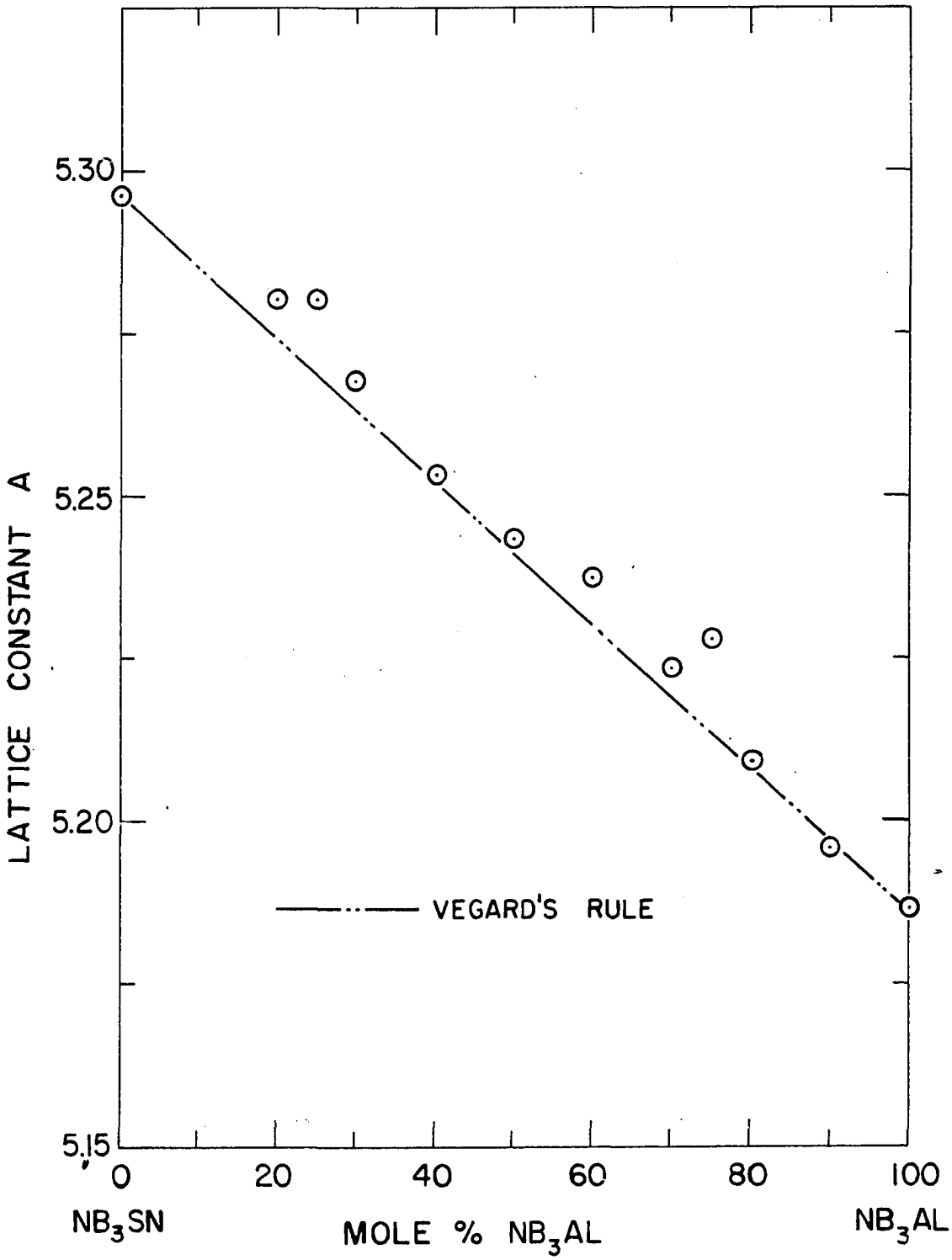
The measurement of the zero field superconducting transformation temperatures for the Nb_3Sn-Nb_3Al alloys did not result in as clear an indication of the superconducting behavior as was anticipated. The data obtained for samples having the same composition but prepared by different methods were somewhat inconsistent. Furthermore, the transition zones observed for most of the alloys were quite broad. These observations suggest that the alloys possibly contained appreciable amounts of interstitial impurities and lacked homogeneity.

The broad transition zones were most likely caused by inhomogeneity of the specimens. The alloys could have contained regions of widely varying compositions. Each individual region would have its own transformation temperature but when measuring a bulk specimen the gross effect would be a gradual increase in the voltage drop across the

specimen over a range of temperatures. Since many of the alloys had transformation zones from the superconducting to the normal state ending above the T_c of Nb_3Sn, it would appear that the T_c of Nb_3Sn can be raised by proper alloying. It may even be possible to form other Cr_3O type mixed crystal compounds that have significantly higher transition temperatures.

The results of the crystallographic study of the Nb_3Sn-Nb_3Al system showed that the two intermetallic compounds were completely miscible. As shown in Figure 26, the lattice constants of individual alloys appear to follow Vegard's rule except in the near vicinity of mole ratios of Nb_3Al in Nb_3Sn of 1:3 and 3:1, where the lattice constants were greater than Vegard's rule would predict. No explanation for this deviation from linearity was apparent. However, there was little doubt that the deviation was real since the experimental errors in the lattice constants of these alloys was less than 5 per cent of the observed deviation.

Figure 26. Plot of lattice constants versus composition for Nb_3Sn-Nb_3Al alloys.


5.30
5.25
5.20
5.15
LATTICE CONSTANT A
VEGARD'S RULE
0
20
40
60
80
100
NB3SN
MOLE % NB3AL
NB3AL

SUMMARY

A proposed constitutional diagram was developed from equilibrium data obtained for the niobium-tin binary alloy system. The equilibrium solubility of niobium in liquid tin varied from 270 ± 20 ppm at 580°C to 1980 ± 20 ppm at 1000°C. The equilibrium solubility of tin in niobium varied from approximately 2.5 w/o tin at 550°C to approximately 3 w/o tin at 1000°C. Two previously unreported intermetallic compounds, Nb_2Sn_3 and Nb_3Sn_2, in addition to Nb_3Sn were found in the system. Nb_3Sn, previously reported by Mattias, et al. (4) decomposed peritectically into niobium and liquid tin at 2125 ± 25°C. Nb_3Sn_2 decomposed peritectically into Nb_3Sn and liquid tin at 915 ± 5°C. Nb_2Sn_3, the assumed but unverified composition for the most tin rich compound, decomposed into Nb_3Sn_2 and liquid tin at 820 ± 3°C.

The crystallographic data obtained for Nb_3Sn_2 and Nb_2Sn_3 are summarized in Table 13.

The intermetallic compounds Nb_3Sn and Nb_3Al were found to be completely miscible in the solid state. All of their alloys were simple cubic (Cr_3O type). Their lattice constants followed Vegard's rule except in the vicinity of mole ratios

of 1:3 and 3:1, where the lattice constants deviated to values larger than was predicted by Vegard's rule.

Alloying of Nb_3Sn with Nb_3Al appears to raise the zero field superconducting transformation temperature of Nb_3Sn slightly.

Table 13. Crystallographic data for Nb_3Sn_2 and Nb_2Sn_3

Compound	Lattice constants	Space group
Nb_3Sn_2	a = 5.637 ± 0.001 A	D_2^8 - I222,
	b = 9.204 ± 0.003 A	D_2^9 - $I2_i2_i2_i$,
	c = 16.677 ± 0.003 A	D_{2h}^{25} - Immm, or
		C_{2v}^{20} - Imm
Nb_2Sn_3	a = 5.72 ± 0.04 A	D_{2h}^{24} - Fddd
	b = 10.03 ± 0.06 A	
	c = 19.01 ± 0.06 A	

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